VOL. XXII. JULY, 1899. NO. 1.

AMERICAN CHEMICAL JOURNAL

Contributions from the Chemical Laboratory of Rose Polytechnic Institute.

XV.—CAMPHORIC ACID.

SIXTH PAPER.

BY WILLIAM A. NOYES.

Reduction of the Neighboring Xylic Acid.

The methods finally used for the synthesis of the neighboring xylic acid $C_6H_3\begin{cases}CH_3 & (1)\\ CO_2H & (2)\\ CH_3 & (3)\end{cases}$, have already been given.[1]

The acid was reduced by amyl alcohol and sodium. The acid was dissolved in four or five times its weight of amyl alcohol in a flask connected with an upright condenser. The solution was heated to boiling and sodium was dropped in, in portions, from the top of the condenser, the total amount used being twice the weight of the acid. More amyl alcohol was also dropped in through the condenser at such a rate as to keep up a moderately vigorous action and prevent the formation of crusts on the sodium or on the bottom of the flask. When the sodium was dissolved, the contents of the flask was allowed to cool slightly, a small amount of water was added, and the amyl alcohol was distilled off with a current of steam. The alkaline solution was cooled, acidified with sulphuric

[1] This JOURNAL, 20, 789.

acid, and extracted twice with ether. The acid obtained by each extraction was dried separately, after distilling away the ether, by heating on the water-bath, reducing the pressure to 30 mm. or less, and shaking vigorously for some minutes. The two portions are dried separately, since the ethereal solution containing the main portion of the acid, takes up much less water than the second, dilute solution. This method of treatment has been found, in many cases, a very quick and satisfactory means of drying substances with boiling-points above 200°.

The residual acid was reduced a second and a third time in the same manner. After the third reduction the alkaline solution was acidified with sulphuric acid, sodium carbonate was added to alkaline reaction, the solution thoroughly cooled, and potassium permanganate added till the pink color was permanent for some minutes. This destroys unsaturated acids which are always present. Some acid sodium sulphite was then added and sulphuric acid, more of the sulphite being used to just dissolve the oxides of manganese in the acid solution. The hexahydro acid was then distilled with steam. Unless too much isovaleric acid has been formed, the acid separates in solid form from the distillate, and after filtering off, washing and drying, it is practically pure. A small additional amount, contaminated with isovaleric acid, from which it can be easily separated, may be obtained by extracting the filtrate. A yield of about 50 per cent was obtained.

Hexahydroxylic Acid, $C_6H_9\begin{cases}CH_3 & (1)\\ CO_2H & (2)\\ CH_3 & (3)\end{cases}$, may be purified by crystallization from ligroin or benzene, in both of which it is very easily soluble. It melts at 72° and boils at 250°-252°. The xylic acid boils at 274°.5.

0.1227 gram of the acid gave 0.1136 gram H_2O, and 0.3117 gram CO_2.

	Calculated for $C_9H_{16}O_2$.		Found.
C_9	108	69.87	69.28
H_{16}	16	10.22	10.29
O_2	32	....	....
	156		

α-Bromhexahydroxylic Acid, $C_8H_{13}\left\{\begin{matrix}CH_2 & (1)\\ CO_2H & (2)\\ Br & \\ CH_2 & (3)\end{matrix}\right.$, was prepared by treating the hexahydro acid with phosphorus pentachloride and bromine.[1] The chloride of the brom acid, prepared in this way, is quite stable toward water, and may even be heated on the water-bath for some time, with a 10 per cent solution of sodium hydroxide, without passing into solution. It is readily decomposed, however, on warming for twenty or thirty minutes with two or three times its weight of glacial formic acid. The acid crystallizes from formic acid, in which it is rather difficultly soluble, in leaflets which melt at 150°-151°. The acid dissolves in a cold solution of sodium hydroxide without decomposition, but on warming the solution it is decomposed, chiefly with the formation of the tetrahydro acid.

0.1076 gram of the acid gave 0.0860 gram AgBr.

	Calculated for $C_8H_{13}BrO_2$.	Found.
Br	34.04	34.01

Δ^1-Tetrahydroxylic Acid.—When the α-brom acid is warmed with alcoholic potash it loses hydrobromic acid and passes over into the Δ^1-tetrahydroxylic acid. This acid is difficultly soluble in water, easily soluble in alcohol and ether. It is much less easily soluble in ligroin than the hexahydro acid but is more easily soluble than the neighboring xylic acid. It separates, on cooling the solution in warm ligroin, in compact crystals which melt at 89°-90°. The conduct of the acid towards potassium permanganate is remarkable. A solution of the acid in sodium carbonate decolorizes that reagent only very slowly and it was at first thought, on that account, that the acid was the hydroxy acid. The analysis, however, left no doubt as to its composition.

0.1473 gram of the acid gave 0.1209 gram H_2O, and 0.3791 gram CO_2.

	Calculated for $C_8H_{14}O_2$.		Found.
C_8	108	70.13	70.19
H_{14}	14	9.09	9.12
O_2	32	....	....
	154		

[1] Baeyer: Ann. Chem. (Liebig), **245**, 175; Aschan: *Ibid.*, **271**, 265.

The properties of the tetrahydroxylic acid, hexahydroxylic acid, and α-bromhexahydroxylic acid leave no possible doubt as to their non-identity with cis-campholytic[1] acid and its derivatives.

Tetrahydroxylic acid melts at 89°-90°, while cis-campholytic acid melts at 133°. The structure of the tetrahydroxylic acid is such that it is highly improbable that the cis-campholytic acid should be a stereomeric modification of the tetrahydroxylic acid.[2] Hexahydroxylic acid melts at 72° and boils at 250°-252°. Dihydrociscampholytic acid is a liquid which boils at 245°-246°. Hexahydroxylic acid is heavier than water and sinks in it. Dihydrociscampholytic acid has the specific gravity 0.9833 at 20°.

The demonstration here furnished of the non-identity of tetrahydroxylic acid and cis-campholytic acid excludes Collie's formula for camphoric acid[3] from further consideration as a possible expression for its structure.

Since this work was undertaken, the synthesis of camphoronic acid by W. H. Perkin, Jr., has furnished a practically complete demonstration that camphoric acid is a derivative of cyclopentane. The low boiling-point and low specific gravity of dihydrociscampholytic acid point strongly in the same direction.

Esterification experiments with the neighboring xylic acid and its hexahydro and tetrahydro derivatives have given results of some interest in their bearing on the constitution of benzene. An account of these is reserved for a later communication.

[1] I retain here the nomenclature which I suggested some time ago, though it has not yet been generally accepted. As was first shown by myself (This JOURNAL, **16**, 501; **17**, 428, 433; **18**, 686; Ber. d. chem. Ges., **28**, 547, 553; **29**, 2326), Walker's campholytic acid and Koenig's and Hoerlin's isolauronolic acid both retain the secondary carboxyl of camphoric acid, and this corresponds to the methylene group of camphor; while Fittig and Woringer's lauronolic acid and Walker's allocampholytic acid (called by myself, almost simultaneously, γ-lauronolic acid) retain the tertiary carboxyl of camphoric acid, corresponding to the carbonyl of camphor. W. H. Perkin, Jr., has very recently (Jour. Chem. Soc. (London), **73**, 815) given a clear statement of a part of these relations and they seem to be thoroughly established. It seems very desirable that these relations should be expressed in the nomenclature and that the two acids with secondary carboxyl should be called campholytic and iso-campholytic (or cis-campholytic), and the two with tertiary carboxyl, lauronolic and iso-lauronolic (or γ-lauronolic). A little temporary confusion appears to the writer better than a perpetuation of the present misleading nomenclature.

[2] For a discussion of a somewhat similar case see this JOURNAL, **18**, 690.

[3] Ber. d. chem. Ges., **25**, 1116.

Mr. J. W. Shepherd, working in this laboratory, has succeeded in obtaining a small amount of the α-hydroxydihydrociscampholytic acid. This, by distillation with lead peroxide and dilute sulphuric acid, has given a ketone, presumably the same as that obtained by Mr. Harris.[1] The study of this ketone has proved to be of more than usual interest and we hope to report upon the matter in the near future.

TERRE HAUTE, April 4, 1899.

CONTRIBUTION TO OUR KNOWLEDGE OF AQUEOUS SOLUTIONS OF DOUBLE SALTS.

II.—CHLORIDES.

BY HARRY C. JONES AND KENJIRO OTA.

The condition of a number of double sulphates in solution in water, has already been studied by Jones and Mackay.[2] They determined the conductivity and freezing-point lowering of the constituent sulphates, then the conductivity and freezing-point lowering of the double sulphate at the same dilution, and by comparing these values, were able to draw conclusions as to the condition of the double salt in the solution.

They found for a number of the alums, that the conductivity and freezing-point lowering of the double salt were less than the sum of these values for the constituents, in the more concentrated solutions. But as the dilution increased the difference became smaller, and at great dilution practically disappeared. They concluded from their measurements of conductivity, upon which, in this case, the greater stress is to be laid, that the complex alum molecules are completely broken down in dilute solution, into the molecules of the simpler sulphates, and that these simpler molecules dissociate as if alone, barring the effect produced on the dissociation when the solutions are not isohydric. But that in concentrated solutions, the difference being much greater than that found in the case of mixtures of sulphates incapable of yielding a double salt, pointed to the conclusion that the alums are partially undecomposed into the constituent molecules in such solutions. The freezing-point determinations pointed to the same conclu-

[1] This JOURNAL, 18, 694. [2] *Ibid.*, 19, 83.

sion, that the alum molecules exist to some extent in the more concentrated solutions.

An article has recently appeared by Macgregor and Archibald,[1] in which the preceding results and conclusions drawn from them are discussed. These authors show how it is possible to calculate the amount of the difference between the conductivity of the double salt and the sum of the conductivities of the constituents, when no double molecules can exist in the mixture of the two salts. We quote a few paragraphs from their paper that their point may be made clear.

"If we mix volumes v_1, v_2 of solutions of electrolytes 1 and 2, which have a common ion, and whose concentrations, ionization coefficients, and molecular conductivities at infinite dilution are, n_1, n_2; α_1, α_2; and $\mu\infty_1$, $\mu\infty_2$, respectively, the concentrations being so low that no appreciable change of volume occurs on mixing, and there being no formation of double salt, and if, after mixing, the ionization coefficients become α'_1, α'_2, respectively, the excess of the actual conductivity over the volume mean conductivity will be

$$[(\alpha'_1-\alpha_1)n_1v_1\mu\infty_1 + (\alpha'_2-\alpha_2)n_2v_2\mu\infty_2]/(v_1+v_2).$$

"This will not vanish unless (1) the solutions are infinitely dilute (all the α's equal to unity), or (2) the solutions are isohydric ($\alpha'_1-\alpha_1$ and $\alpha'_2-\alpha_2$ both equal to zero), or (3) the change of ionization and other quantities involved are appropriately related to one another."

They then proceed to calculate what the differences would be if no double salt existed in solution.

"For this purpose the $\mu\infty$'s and the α's of the above expression must be determined. The former may be found from the determinations of ionization coefficient and molecular conductivity made by Jones and Mackay. * * * The values which the ionization coefficients would have in the alum solutions, on the assumption of the presence of no double molecules, may be determined from the values of the ionization coefficieuts of the simple solutions observed by Jones and Mackay, by the method described by one of us in a former paper,[2] though the data are somewhat meagre for the purpose, and the results must therefore be used with caution.

[1] Phil. Mag., 46, 509. [2] *Ibid.*, [5], 41, 276.

"Having obtained the requisite data in the ways indicated, we have calculated the amounts by which the conductivities of the alum solutions should differ from the arithmetic means of the conductivities of their mixture constituents, if no double salt were present as such; and we find that for solutions of $KAl(SO_4)_2$ and $KCr(SO_4)_2$, of dilution 12 litres per gram-molecule, the molecular conductivity should be less than the arithmetic mean of the molecular conductivities of the mixture constituents by about 0.4 and 0.7 per cent respectively. Jones and Mackay found that for these solutions the molecular conductivity was less than the arithmetic mean by 2.6 and 8.8 per cent respectively. Assuming that the available data are sufficient for the calculation, it is obvious not only that the conclusion of these observers with respect to the chromium alum seems to be substantiated, but that in the case of the potash alum, also, the result is such as would be accounted for by the existence of double salt in solution."

Jones and Mackay studied, also, one of the double chlorides, that of potassium and zinc, using the conductivity method in the same manner as with the double sulphates. As the results of their investigation upon this substance have not yet been published they are recorded in this place.

Rüdorff[1] distinguished two classes of double chlorides. Those which suffer decomposition in water solution, and those which remain undecomposed. The first class are to be regarded as double salts of the same type as the alums. The second class he regards as true binary compounds. The following examples of the first class are given:

$$2KCl + CuCl_2 + 2H_2O,$$
$$2NH_4Cl + CuCl_2 + 2H_2O,$$
$$2KCl + ZnCl_2 + H_2O,$$
$$KCl + MgCl_2 + 6H_2O,$$
$$2NaCl + CdCl_2 + 3H_2O,$$
$$BaCl_2 + CdCl_2 + 4H_2O.$$

It seemed of interest to study an example of this class by the conductivity method. For this purpose the double chloride of potassium and zinc was selected.

[1] Ber. d. chem. Ges., **21**, 3048 (1888).

Preparation.

In preparing the double chloride of potassium and zinc, potassium chloride, which had been twice crystallized, and was shown by the flame test to be free from sodium, was used. The zinc chloride used was tested and found to be free from impurities. The two chlorides were brought together in solution in the proportion necessary to form the double salt, and the solution evaporated to crystallization. The salt was separated as rapidly as possible from its mother-liquor, by the filter-pump, and dried under a press. A specimen dried at 130° was analyzed for zinc.

The analysis gave :

Percentage of zinc found	22.91
" calculated for $2KCl.ZnCl_2$	22.94

Conductivity Results obtained by Jones and Mackay for $2KCl.ZnCl_2$.

Volume. v.	μ_v at 25°. 1st series.	μ_v at 25°. 2nd series.	Mean of 1 and 2.
1.0	176.0	....	176.0
2.0	244.2	....	244.2
4.0	303.7	....	303.7
20.0	397.4	397.2	397.3
40.0	426.2	423.8	425.0
200.0	468.4	469.0	468.7
400.0	483.2	484.2	483.7
2000.0	504.0	504.6	504.3
4000.0	510.8	512.3	511.5
20000.0	516.8	509.0	512.9
40000.0	518.8	516.0	517.4

A comparison of the conductivity of the double salt with the conductivities of its constituents is given below. The values for zinc chloride and potassium chloride are interpolated from the tables of Kohlrausch,[1] and the temperature coefficient added, so that they obtain at 25°. The molecular conductivity of the zinc chloride is taken at the same volume as the double salt. That of potassium chloride is taken as twice the molecular conductivity of potassium chloride at one-half the volume of the double salt.

[1] Ann. d. Phys. (Wied.), **26**, 161 (1885).

Double Chloride of Zinc and Potassium.

Volume v of KCl.	KCl $2\mu_v$ 25°.	Volume v of $ZnCl_2$.	$ZnCl_2$. μ_v 25°.	Sum.	$2KCl.ZnCl_2$ observed. μ_v 25°.	Difference.
0.5	196.0	1.0	78.4	274.4	176.0	98.4
1.0	211.8	2.0	120.0	331.8	244.2	87.6
2.0	221.6	4.0	140-3	361.9	303.7	58.2
10.0	241.4	20.0	179.2	420.6	397.3	23.3
20.0	250.0	40.0	186.7	436.7	425.3	11.4
100.0	264.8	200.0	213.6	478.4	468.7	9.7
200.0	269.0	400.0	220.1	489.1	483.7	5.4
1000.0	275.4	2000.0	232.0	507.4	504.3	3.1
2000.0	277.6	4000.0	234.8	512.4	511.5	0.9
10000.0	279.0	20000.0	240.2	519.2	512.9	6.3
20000.0	280.0	40000.0	240.7	520.7	517.4	3.3

The foregoing comparison leaves no room for doubt as to the existence of this double salt as such in concentrated solution, while at a dilution of between 1000 and 2000 liters it is entirely dissociated into its constituents.

Conclusion.

Regarding the double chloride of zinc and potassium as a type of the class of dissociated double halides, the conclusion was drawn that these salts are present as such in their concentrated solutions. As compared with the alums, they show a greater degree of stability towards water in concentrated solutions, but, in dilute solutions, resemble them in becoming wholly dissociated into their component salts.

We have continued the investigation upon the double chlorides, thinking it desirable that a number of compounds should be studied. We at first repeated the above work on the double chloride of zinc and potassium. The compound was prepared and analyzed in exactly the same manner as described above. A standard solution was prepared and from this, directly or indirectly, all of the more dilute solutions were made. The conductivity measurements were made at 25°, so that the data are directly comparable with those given above. All of the water used in preparing the solutions was carefully purified by distilling from chromic acid and alkaline potassium permanganate, as already described.[1] We obtained the fol-

[1] Zischr. phys. Chem., 22, 237.

lowing results for the conductivity of the double salt, which are compared with the sum of the conductivities of the constituents, given in the preceding table. The differences given below are directly comparable with the differences in the above table:

$2KCl.ZnCl_2$.

Volume v.	μ_v at 25°.	Difference.
1.0	172.6	101.8
2.0	241.3	90.5
4.0	298.5	63.4
20.0	391.5	29.1
40.0	423.6	13.1
200.0	470.4	8.0
400.0	484.8	4.3
2000.0	510.5	—3.1
4000.0	512.0	0.4
20000.0	518.0	1.2
40000.0	520.0	0.7

Our results confirm those previously obtained, the slight differences being unquestionably due to experimental error.

We next prepared the double chloride of potassium and cadmium, $KCl.CdCl_2$, by bringing the constituent chlorides together in the proportion to form the double salt. The solution was carefully evaporated, the double salt separating without serious difficulty. It, however, requires more care to obtain this salt in pure condition than to obtain the corresponding zinc salt. The compound was freed from the mother-liquor by pressing between drying paper, and analyzed. The cadmium was determined by the carbonate method, with the result that the compound was shown to be pure. The results of the conductivity measurements of solutions of this salt are given in the following table, together with a comparison with the sum of the conductivities of the constituent chlorides.

Results for $KCl.CdCl_2$.

Volume v.	KCl μ_v, 25°.	$CdCl_2$ μ_v, 25°.	Sum.	$KCl.CdCl_2$ μ_v at 25°.	Difference.
2	111.27	46.88	158.15	116.35	41.80
4	113.74	64.70	178.44	144.42	34.02
8	118.68	83.27	201.95	171.79	30.16
16	122.33	102.55	224.88	198.18	26.70
32	125.91	122.09	248.00	223.87	24.13
64	127.97	143.13	271.10	250.53	20.57
128	130.80	163.55	294.35	276.21	18.14
256	132.28	182.21	314.49	303.03	11.46
512	133.99	197.94	331.93	325.45	6.48
1024	134.79	212.28	347.07	346.83	0.24

The double chloride of sodium and aluminium was particularly inviting for our work, since it is stated that this compound can be volatilized by heat, without decomposition. This substance is, thus, far more stable with respect to heat than other substances of its class, and it was therefore especially interesting to see whether it would show a corresponding relative stability with respect to water.

Several attempts were made to prepare the compound in quantity by the methods described, but none of them gave us a yield sufficient for our purpose. We then determined to mix solutions of the two chlorides in quantities just sufficient to form the double salt. The chloride of aluminium was prepared by dissolving pure aluminium hydroxide in hydrochloric acid, using a very slight excess of the hydroxide. The aluminium hydroxide was precipitated from pure potassium alum by ammonia, and the precipitate washed until it was free from potassium and ammonia. The hydroxide was washed by boiling the precipitate with large quantities of water, allowing it to settle, and successively decanting and filtering. The results obtained are given below:

Results for $NaCl.AlCl_3$.

Volume v.	NaCl μ_v, 25°.	$AlCl_3$ μ_v, 25°.	Sum.	$NaCl.AlCl_3$ μ_v, 25°.	Difference.
2.88	93.55	169.48	263.03	228.64	34.39
5.76	97.44	196.65	294.09	269.05	25.04
11.52	103.65	217.76	321.41	297.82	23.59
23.04	106.89	237.00	343.89	325.82	18.07
46.08	109.46	254.33	363.79	349.10	14.69
92.16	112.19	271.71	383.90	370.34	13.56
184.32	114.26	289.19	403.45	394.75	8.70
368.64	115.59	307.32	422.91	414.50	8.40

We then turned our attention to the double chloride of ammonium and mercury, ($2NH_4Cl.HgCl_2$). Mercuric chloride is, as is well known, very slightly dissociated by water. We wished to see whether results of the same general order as the above would be obtained, when one of the constituent chlorides remained in the solution for the most part in the molecular condition.

The double salt was prepared by bringing the constituent chlorides together in the proportion to form the salt, and carefully evaporating the solution until the double salt separated. The salt was quickly pressed between drying paper and analyzed. Analysis showed that the product which we used was pure. A solution of the strength desired was standardized, and from this all of the remaining solutions were prepared. The conductivity results obtained are given below :

Results for $2NH_4Cl.HgCl_2$.

Volume v.	NH_4Cl $2\mu_v$ 25°.	Volume v.	$HgCl_2$ μ_v 25°.	Sum.	$2NH_4Cl.HgCl_2$ μ_v 25°.	Difference.
2.5	221.7	5	0.79	222.49	195.5	26.99
5.0	230.0	10	1.17	231.17	213.0	18.17
10.0	238.64	20	1.60	240.24	227.73	12.51
20.0	247.24	40	2.48	249.72	240.68	9.04
40.0	252.64	80	3.80	256.44	251.93	4.51
80.0	257.52	160	6.02	263.54	260.70	2.84

Discussion of the Results.

It will be readily understood why twice the molecular conductivity of ammonium chloride, at one-half the dilution, is taken in the above table, if we consider that in the double salt there are two molecules of ammonium chloride to one of mercury chloride. The dilutions are so taken that they can be compared directly with the dilutions which we obtain in the solution of the double salt. These same remarks apply to the potassium chloride in the double salt with zinc, where there are two molecules of potassium chloride to one of zinc chloride. Before considering the final results obtained, it should be stated that the values of μ_v for potassium chloride, sodium chloride, and ammonium chloride, were obtained from the results of Kohlrausch's conductivity measurements, by interpo-

lation ; the temperature coefficient being added in each case, transforming the results at 18° into results at 25°.

The values of the differences for the double chloride of potassium and cadmium are smaller than for the corresponding zinc salt at the same dilution, yet the same general relation obtains. The difference is largest in the most concentrated solution, and becomes smaller as the dilution increases, reaching zero at about 0.001 normal. It should be stated that our conductivity values for cadmium chloride differ appreciably from those of Grotrian.[1]

The differences are of the same order for the sodium aluminium chloride as for potassium cadmium chloride ; indeed, they are slightly less in the former case. The greater stability of the sodium aluminium chloride with respect to heat, therefore, does not manifest itself with respect to water. This compound is more dissociated in aqueous solution than substances of the same class which cannot be volatilized without decomposition.

The differences for the ammonium mercuric chloride are smaller, for the same dilution, than for either of the double chlorides thus far studied.

A comparison of the results obtained with the double sulphates with the results of this work, shows a much greater difference in the latter, between the sum of the conductivities of the constituents and the conductivity of the double salt. While this amounted at most to a few per cent with the alums, it is as great as 40 per cent for the double chloride of potassium and zinc, 26 per cent for the corresponding cadmium salt, 13 per cent for the double chloride of sodium and aluminium, and 12 per cent for the double chloride of ammonium and mercury. These differences for the double chlorides, as for the double sulphates, vanish at great dilution.

The conclusion that molecules of double salts exist in the more concentrated solutions, can be drawn with much greater confidence for the double chlorides than for the double sulphates. The former, under these conditions, are far more resistant to the dissociating action of water, than the latter.

It should be stated that this conclusion is directly in accord

[1] Ann. d. Phys. (Wied.), 18, 177 ; Ztschr. phys. Chem., 3, 481.

with the view of Remsen, that the double halides are to be regarded as well-defined chemical compounds. As measured by their power to resist the dissociating action of water, if the alums are chemical compounds, so much the more must we regard the double chlorides as such.

We attempted to apply the freezing-point method to the double chlorides, as had already been done in the case of the double sulphates. The results obtained were, however, not satisfactory. Work is now in progress in this line.

The study of other examples of double halides is now being made in this laboratory by Dr. Knight. We propose to examine by the conductivity, and perhaps the freezing-point method, a number of classes of double salts.

CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
January, 1899.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON UNDECYLAMINE AND PENTADECYLAMINE AND THE PREPARATION OF THE HIGHER AMINES OF THE ALIPHATIC SERIES[1].

BY ELIZABETH JEFFREYS.

Hofmann's[2] method of preparing amines by the action of bromine and potassium hydrate upon acid amides in aqueous solution according to

$$RCONH_2 + Br_2 + 4KOH = RNH_2 + 2KBr + K_2CO_3 + 2H_2O,$$

furnishes very good yields of the lower aliphatic amines, but as the molecular weight of the acid amide increases the yield of amine diminishes. This is due particularly to two secondary reactions, in one of which the bromine and alkali act upon the amines formed and produce nitrils according to the equation:

$$RCH_2NH_2 + 2Br_2 + 4NaOH = RCN + 4NaBr + 4H_2O.$$

By distilling the amine with steam as soon as it is formed, Hoogewerff and Van Dorp[3] succeeded in preventing the formation of nitrils.

[1] Vide also a preliminary report, Ber. d. chem. Ges., **30**, 898.
[2] Hofmann: Ber. d. chem. Ges., **15**, 762.
[3] Hoogewerff and Van Dorp: Rec. trav. chim., **6**, 387.

In the other secondary reaction by which the yield of amine is diminished, acyl-alkylureas are formed:

$$2RCONH_2 + Br_2 + 2KOH = RNHCONHCOR + 2KBr + 2H_2O.$$

With increasing molecular weight of the acid amide, the formation of these acylureas is favored and in the higher series they are the chief product of the action of bromine and aqueous alkali on acid amides. By saponifying such ureas amines can be obtained, but the yield is small.

Amines higher in the series than heptylamine cannot be obtained with good yields by the Hofmann method. To prepare octylamine, Hoogewerff and Van Dorp[1] distilled the bromamide with lime and obtained 45 per cent of the theoretical yield of amine. This method involves the preparation of the bromamide and, as shown below, this is one of the main difficulties to overcome in the higher aliphatic series. Hoogewerff and Van Dorp's method in modified form is hardly feasible, therefore, for preparing amines of very high molecular weight.

Turpin[2] prepared heptadecylamine, $CH_3(CH_2)_{16}NH_2$, by converting stearic amide by means of aqueous potassic hydrate and bromine into stearyl-heptadecylurea and distilling the urea with lime. As but half the urea molecule is of avail in preparing the amine, the yield obtained was necessarily low (22 grams of heptadecylamine from 100 grams of stearamide), and as a ketone, stearon, is also formed in the same reaction, the isolation of the pure amine involves a tedious process.

Lengfeld and Stieglitz[3] having found that sodium methylate in methyl alcohol solution converts acid bromamides into urethanes according to

$$RCONHBr + CH_3ONa = CH_3NHCOOCH_3 + NaBr,$$

the work described in this paper was undertaken at the suggestion and carried on under the direction of Professor Stieglitz, to determine whether this reaction could not be utilized as a convenient method of preparing higher aliphatic amines, and also to determine, if possible, why, in the

[1] Rec. trav. chim., **6**, 387. [2] Ber. d. chem. Ges., **21**, 2488.
[3] This JOURNAL, **15**, 215, 504; **16**, 270.

Hofmann reaction, the formation of ureas of the higher aliphatic series should be more favored than those of lower molecular weight.

The investigation was carried on by the use of palmitic, stearic, and lauric amides. All attempts to prepare palmitic and stearic bromamides proved unsuccessful.

The chloramides were, however, prepared with considerable difficulty and converted by treatment with sodium methylate into urethanes. As the preparation of the chloramides proved so difficult, an attempt was made to effect a rearrangement of the amides in alcohol solution without the isolation of the chlor- or bromamides.

The experiments proved successful, urethanes being formed in almost quantitative yield according to

$$RCONH_2 + Br_2 + 2NaOCH_3 = RNHCOOCH_3 + 2NaBr + HOCH_3.$$

As amines were obtained in excellent yield when the urethanes were distilled with lime, the investigation has proved entirely satisfactory in leading to as convenient a method of preparing the higher aliphatic amines, as that employed in obtaining the lower amines.

From the easily accessible lauric and palmitic amides, the hitherto unknown normal undecylamine and normal pentadecylamine were prepared in considerable quantity; and from undecylamine, undecyl alcohol, also heretofore unknown, was prepared.

In regard to the second object of investigation, it was soon found that in order to prevent the formation of urea, it is necessary that a rearrangement shall take place quickly, almost instantaneously, throughout the whole mass. In working with lauric amide, it was found necessary to mix the substances together as quickly as possible. When the sodium alcoholate solution was poured in small quantities into the flask containing the solution of amide and bromine, two-thirds of the product was found to be urea. The same result was obtained when the amide and sodium alcoholate solutions were mixed together and the bromine added, drop by drop, to the mixture. If, on the other hand, the sodium alcoholate solution was poured, all at once, into the bromine

and amide solution, almost a quantitative yield of urethane was obtained.

Apparently when the reaction proceeds slowly, one molecule of the bromamide after suffering the Beckmann rearrangement, unites at once with a second molecule of acid amide which is still present under those conditions, to form urea according to:

$$RCONHBr + RCONH_2 + NaOCH_3 \rightarrow RCONHCONHR + NaBr + HOCH_3,$$

rather than with the alcohol to form a urethane.

The cause, therefore, of the formation of ureas when the higher amides are treated with bromine and aqueous alkali, according to Hofmann's method, lies undoubtedly in the fact, that, on account of their difficult solubility in aqueous solvents, the rearrangement of the acid amide takes place so slowly that there is always present a sufficient amount of amide to form a urea.

The inevitable conclusion to be drawn from the facts given was rather surprising, inasmuch as isocyanates, the probable intermediate products[1] in the Beckmann rearrangement,[2] under ordinary conditions, react much more readily with alcohols than with acid amides. Experiments were made by treating benzamide, in methyl alcohol solution, with phenyl isocyanate under varying conditions, and they invariably resulted in the formation of methylphenylurethane, not a trace of phenylbenzoylurea being formed.

According to Hoogewerff and Van Dorp bromformamides are the first intermediate products of the Beckmann rearrangement of acid bromamides, but chlorformanilide with a methyl alcohol solution of benzamide, under varying conditions, did not give any more phenylbenzoylurea than the isocyanate itself.[3]

The new method of converting acid amides into urethanes, by the action of bromine and sodium methylate, was found

[1] Hofmann: Ber. d. chem. Ges., **15**, 412. [2] Stieglitz: This JOURNAL, **18**, 751.

[3] The question raised will be further investigated as it promises to throw more light on the theory of the Beckmann rearrangement of acid bromamides. Mr. Yates is studying the action of undecyl isocyanate on lauric amide, as lauric amide seems to show a marked tendency to form undecyllaurylurea when subjected to the action of the rearranging reagents.

also to be applicable to the amides of the aromatic series. Since much time and labor are saved and the loss involved in the isolation of the dry bromamides is prevented, we can now class the urethanes among the most easily accessible bodies.

This method was also tried in cases where the old method had either failed entirely or given poor results. The yields of urethanes obtained in ethyl alcohol solution were very much higher than those obtained by Swartz,[1] by the older method, but all attempts to effect a rearrangement of unsaturated acid amides, $RCH:CHCONH_2$, failed, because the unsaturated group is more reactive than the acid amide group.

For a similar reason salicylic amide, on account of the activity of the hydrogen of the benzene ring, due to the presence of the hydroxyl group, undergoes no rearrangement until the benzene ring has been brominated.

Experimental Part.

That acid chloramides can be used instead of acid bromamides in effecting the rearrangement to urethanes, was shown by the action of sodium methylate on benzchloramide. 1.2 gram (1 mol.) of benzchloramide was added to a solution of sodium methylate, obtained by dissolving 0.3 gram (2 atoms) of sodium in 12 grams of pure methyl alcohol. The reaction was complete after heating the mixture about five minutes on the water-bath. The excess of alkali was neutralized by acetic acid, the alcohol distilled and the residue recrystallized from hot water. The product obtained was identified by its melting-point (47°) and other properties as methylphenylurethane. The reaction takes place exactly as when benzbromamide is used.[2]

Palmitic Chloramide, $C_{15}H_{31}CONHCl$.—On account of the difficult solubility of palmitic amide, it was impossible to prepare palmitic bromamide, but the chloramide can be obtained in almost pure condition as follows: 10 grams of palmitic amide dissolved in about 400 cc. of alcohol were poured into about five times the calculated amount of hypochlorous acid, the acid having been prepared by passing chlorine into a 15 per cent solution of sodium carbonate, kept at a temperature of

[1] This JOURNAL, 19, 295. [2] Ber. d. chem. Ges., 19, 2274.

about —5°. A white precipitate was immediately formed, this being, evidently, the palmitic amide precipitated by the cold hypochlorous acid solution. Upon shaking the flask vigorously for a few minutes considerable heat was developed and the precipitate redissolved. On cooling, a white precipitate was deposited; this was filtered immediately and washed with a little ice-cold water. After it was dried on a clay plate for two or three hours, a chlorine determination was made by adding potassium iodide to an alcoholic solution of the chloramide, and acidifying and titrating with thiosulphate, the iodine being liberated according to:

$$C_{15}H_{31}CONHCl + 2HI = C_{15}H_{31}CONH_2 + HCl + 2I.$$

I. 0.2046 gram substance gave 0.0238 gram chlorine.

II. 0.2026 gram substance gave 0.0236 gram chlorine.

	Calculated for $C_{16}H_{32}NOCl$.	Found. I.	II.
Cl	12.26	11.65	11.65

Palmitic chloramide melts at 70°–71°. It is insoluble in water, difficultly soluble in cold alcohol and ligroin and readily soluble in benzene, chloroform and ether. The yield is almost quantitative.

Methyl Pentadecylcarbamate, $C_{15}H_{31}NHCO_2CH_3$, *from Palmitic Chloramide*.—To convert palmitic chloramide into urethane 5 grams of it was treated with 0.45 gram of sodium dissolved in 18 grams of methyl alcohol. The chloramide dissolved immediately in the alkaline solution, but it was necessary to boil the solution for twenty minutes before the action was complete. After distilling off the alcohol, the product remaining was washed with water and recrystallized from hot alcohol.

I. 0.4406 gram at 739.8 mm. and 23.5° gave 19.8 cc. nitrogen.

II. 0.4568 gram at 744.7 mm. and 22.5° gave 21.3 cc. nitrogen.

III. 0.1992 gram gave 0.5208 gram CO_2, and 0.2274 gram H_2O.

	Calculated for $C_{15}H_{31}NHCO_2CH_3$.	Found. I.	II.
N	4.91	4.92	5.16
C	71.57	71.30	..
H	12.28	12.68	..

Methylpentadecylurethane is difficultly soluble in cold ligroin and in alcohol, but readily soluble in ether, chloroform and benzene. It crystallizes in leaflets and melts at 61°–62°.

Preparation of Urethanes Directly from Amides.

As the isolation of the chloramide proved to be very difficult, the following experiments were made to convert acid amides directly into urethanes without isolating the chlor- or bromamides.

Methyl Phenylcarbamate, $C_6H_5NHCOOCH_3$.—A solution of 3.8 grams (2 equiv.) of sodium in 95 grams of methyl alcohol was poured into a flask containing 10 grams of benzamide (1 equiv.), dissolved in 51 grams of methyl alcohol, and to this mixture, 13.2 grams (2 equiv.) of bromine were added. Some action took place in the cold, but it was necessary to heat the mixture for twenty minutes before the action was complete.

After recrystallization from hot water 5.9 grams of pure urethane were obtained. The reaction takes place in the same manner when the sodium methylate solution is added to the mixture of amide and bromine solution.

Methyl m-Nitrophenylcarbamate, $NO_2C_6H_4NHCOOCH_3$.—3.8 grams (1 equiv.) of *m*-nitrobenzamide were dissolved in 16 grams of methyl alcohol, and to this were added 4 grams (2 equiv.) of bromine and 1.1 gram (2 equiv.) of sodium dissolved in 28 grams of methyl alcohol. The alcohol was allowed to evaporate at ordinary temperature and the residue shaken up with hydrochloric acid, to remove the small quantity of *m*-nitraniline formed, and then recrystallized from chloroform. The urethane was recognized by its crystal form and melting-point (147°–149°) as being identical with the one obtained by Folin.[1] The yield obtained was 91 per cent of theory.

Methyl Pentadecylcarbamate, $C_{15}H_{31}NHCOOCH_3$, *from Palmitic Amide.*—25.5 grams (1 mol.) of palmitic amide, dissolved by warming in 69 grams of methyl alcohol, were mixed with a solution of 4.6 grams (2 atoms) sodium in 115 grams of methyl alcohol and 16 grams (1 mol.) of bromine added.

[1] Folin: This JOURNAL, 19, 323.

The mixture was heated on the water-bath for about ten minutes. After adding a few drops of acetic acid to neutralize the excess of alkali, the alcohol was distilled off, and the remaining product washed thoroughly with water to remove the sodium bromide. It was then dissolved in ligroin to separate the urethane from some unchanged palmitic amide (m. p. 104°), which is difficultly soluble in ligroin. When recrystallized twice from alcohol, the urethane melted at 61°–62°, agreeing with that of the pentadecylurethane obtained by the action of sodium methylate upon palmitic chloramide. The yield is 83–94 per cent of the calculated quantity.

Its identity was further shown by an analysis.

0.383 gram at 752.6 mm. and 21.5° gave 17.9 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOOCH_3$.	Found.
N	4.91	5.25

Normal Pentadecylamine, $CH_3(CH_2)_{14}NH_2$.—Pentadecylamine can be prepared by heating pentadecylurethane with concentrated hydrochloric acid (five hours in a sealed tube to 200°) or with concentrated sulphuric acid (one hour to 110°–120° in an open flask) and then heating with alcoholic potash and distilling. The best method of preparing the amine is to distil the urethane with about three and one-half times its weight of slaked lime, the amine being obtained quantitatively according to the equation :

$$C_{15}H_{31}NHCOOCH_3 + Ca(OH)_2 = C_{15}H_{31}NH_2 + CaCO_3 + CH_3OH.$$

Pentadecylamine Hydrochloride, $CH_3(CH_2)_{14}NH_3Cl$.—This salt is best prepared by dissolving the free amine (obtained by distilling pentadecylurethane with lime) in alcohol, adding an excess of concentrated hydrochloric acid, and evaporating to dryness on the water-bath. It was purified by washing it thoroughly with ether, then dissolving it in a small quantity of alcohol and precipitating with ether.

I. 0.3446 gram substance at 750.3 mm. and 23° gave 17.2 cc. nitrogen.

II. 0.4086 gram substance at 747 mm. and 16° gave 19.5 cc. nitrogen.

III. 0.2788 gram substance gave 0.6990 gram CO_2, and 0.328 gram H_2O.

IV. 0.2244 gram substance gave 0.5604 gram CO_2, and 0.2659 gram H_2O.

	Calculated for $C_{15}H_{31}NH_2Cl$.	Found. I.	II.
N	5.31	5.55	5.43
C	68.31	68.37	68.10
H	12.90	13.07	13.16

Pentadecylamine hydrochloride crystallizes in glistening leaflets; it is very soluble in alcohol, but insoluble in ether, ligroin, and water. It decomposes without melting at 200°.

Pentadecylamine Chlorplatinate, $(C_{15}H_{31}NH_2)_2PtCl_6$, was prepared by adding a solution of chlorplatinic acid to an alcoholic solution of pentadecylamine. A yellow body was precipitated which is slightly soluble in alcohol, insoluble in water and decomposes without melting when heated above 205°.

0.5356 gram gave 0.1218 gram of platinum.

	Calculated for $(C_{15}H_{31}NH_2)_2PtCl_6$.	Found.
Pt	22.57	22.73

Monopentadecylurea, $C_{15}H_{31}NHCONH_2$. — The monourea furnishes an easy method for the rapid and certain identification of pentadecylamine or its hydrochloride. Molecular quantities of pentadecylamine hydrochloride dissolved in alcohol, and potassium cyanate, dissolved in as small a quantity of water as possible, were mixed together and evaporated to dryness on the water-bath. The compound formed was washed with water and recrystallized from hot alcohol.

0.2158 gram substance at 747.1 mm. and 21.5° gave 20.2 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCONH_2$.	Found.
N	10.37	10.45

Monopentadecylurea is a white substance crystallizing in leaflets and melting at 109°; it is insoluble in ligroin but readily soluble in hot alcohol. It was used most frequently in identifying the new amine.

Pentadecylamine, $CH_3(CH_2)_{14}NH_2$.—The free amine is best prepared as follows: 70 grams of lime, to which has been added 30 grams of water and 20 grams of pentadecylurethane are thoroughly mixed together and distilled from a porcelain, or hard glass retort of 300 cc. capacity. The receiver was kept in cold water. The product formed was dissolved in ligroin, and dried with caustic potash. The ligroin solution was separated from the caustic potash by filtering it with a siphon filter. The amine was then heated on the water-bath for a couple of hours over sodium, and finally distilled over sodium into a second distilling-flask, from which it was redistilled.

I. 0.3488 gram at 751.8 mm. and 13.7° gave 17.1 cc. nitrogen.

II. 0.4186 gram at 735.4 mm. and 15.5 gave 21.1 cc. nitrogen.

	Calculated for $C_{15}H_{31}NH_2$.	Found. I.	II.
N	6.16	5.75	5.69

When the free amine is weighed it absorbs carbon dioxide and water from the air with such avidity that it is impossible to get very good figures. In order to obtain a more exact analysis, the specimen analyzed was converted into the hydrochloride, and a determination of the hydrogen, carbon and nitrogen made (see second analysis of pentadecylamine hydrochloride).

Pentadecylamine is a white substance crystallizing in leaflets, melting at 36.5° and boiling at 298°–301° at ordinary pressure; it has a peculiar odor, dissolves in all the organic solvents, and combines with acids, but does not dissolve in them. By working carefully, almost a quantitative yield can be obtained.

Benzoylpentadecylamine, $C_{15}H_{31}NHCOC_6H_5$.—A calculated quantity (1 mol.) of benzoyl chloride was added to an ether solution of pentadecylamine (2 mol.). In order to get all the amine in solution, it was necessary to heat it to drive off any carbon dioxide absorbed, as the carbonate is not soluble in ether. The ether mixture was shaken up with a weak solution of caustic soda and when no further odor of

benzoyl chloride was perceptible, it was washed two or three times with water and the ether distilled.

The compound obtained crystallizes in needles and melts at 78°; it is soluble in ether, alcohol and benzene.

For analysis it was recrystallized from benzene.

I. 0.4552 gram substance at 743.3 mm. and 17° gave 18.2 cc. nitrogen.

II. 0.4368 gram substance at 746.1 mm. and 17.3° gave 17.1 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOC_6H_5$.	Found. I.	II.
N	4.22	4.59	4.44

All the analytical data obtained for the compound formed when pentadecylurethane is distilled with slacked lime, as well as those obtained for its derivatives, indicate that it is a primary amine formed according to:

$$C_{15}H_{31}NHCO_2CH_3 + Ca(OH)_2 = C_{15}H_{31}NH_2 + CaCO_3 + HOCH_3.$$

As Nölting[1] observed that methylphenylurethane, $C_6H_5NHCO_2CH_3$, gives on distilling with lime (unslacked) monomethylaniline according to:

$$C_6H_5NHCO_2CH_3 + CaO = C_6H_5NHCH_3 + CaCO_3,$$

and the analytical figures for derivatives of pentadecylamine, $C_{15}H_{31}NH_2$, and methylpentadecylamine, $C_{15}H_{31}NHCH_3$, lie rather close together, some reactions were tried which prove beyond any doubt that the amine prepared by me is a primary amine; with carbon disulphide it gives a mustard oil, $C_{15}H_{31}N{=}CS$; by the action of phosgene the isocyanate, $C_{15}H_{31}NCO$, is obtained and by the action of sodium nitrite on the hydrochloride of the amine, it is converted into normal primary pentadecyl alcohol, $C_{15}H_{31}OH$.

Pentadecylamine Pentadecyl Dithiocarbamate, $(C_{15}H_{31}NH)CS_2NH_2C_{15}H_{31}$, was obtained when an excess of carbon disulphide was added to an ether solution of pentadecylamine. A white precipitate was at once formed, which, when filtered and dried, melted at 99°. The substance was not analyzed, but was heated in a sealed tube for twenty hours at 100°.

[1] Ber. d. chem. Ges., **21**, 3155.

Hydrogen sulphide was split off, and the dithiocarbamate converted into dipentadecylthiourea according to :

$$(C_{15}H_{31}NH)CS_2NH_2C_{15}H_{31} = (C_{15}H_{31}NH)_2CS + H_2S.$$

Dipentadecylthiourea was recrystallized by dissolving it in alcohol and precipitating it with water. It melts at 88·5°.

0.2142 gram gave 0.0984 gram barium sulphate (Carius' method).

	Calculated for $(C_{15}H_{31}NH)_2CS$.	Found.
S	6.45	6.30

Pentadecyl Mustard Oil, $C_{15}H_{31}NCS$, was prepared by heating pentadecylamine in solution in absolute alcohol with an excess of carbon disulphide :

$$C_{15}H_{31}NH_2 + CS_2 = C_{15}H_{31}NCS + H_2S.$$

This simple method seems to be a general one for preparing mustard oils from the higher aliphatic amines, since it succeeded with pentadecylamine as well as with heptadecylamine.[1] It was necessary to boil the alcoholic mixture for two days, at the end of which time no further odor of hydrogen sulphide could be detected. On evaporating the alcohol, a solid and an oil remained in the flask. The oil was dissolved in ligroin, and the solid remaining undissolved was identified as dipentadecylthiourea (m. p. 88.5°). As the oil was found to be impure and as it decomposes on distilling *in vacuo*, no analysis of the compound could be obtained, but it was identified as being chiefly pentadecyl mustard oil, $C_{15}H_{31}NCS$, by its action on amines. With aniline it gives phenylpentadecylthiourea according to :

$$C_{15}H_{31}NCS + C_6H_5NH_2 = C_{15}H_{31}NHCSNHC_6H_5,$$

and warmed with pentadecylamine, it yields dipentadecylthiourea.

Phenylpentadecylthiourea, $C_{15}H_{31}NHCSNHC_6H_5$, was obtained when molecular quantities of the mustard oil, dissolved in alcohol and aniline, were mixed together, and the solution boiled for ten or fifteen minutes on the water-bath. A few drops of acetic acid were added and the alcohol distilled. After recrystallizing the residue several times from alcohol, the thiourea obtained was found to melt at 79°.

[1] Turpin : Ber. d. chem. Ges., 21, 2486.

The same compound was also prepared by adding to pentadecylamine the calculated amount of phenyl mustard oil, and heating the mixture for a few minutes on the water-bath. After recrystallizing from alcohol, the substance obtained by this method was found to melt at 79°. A mixture of the two melted sharply at 79°, showing them to be identical and leaving no doubt as to the constitution of the thiourea.

0.267 gram substance at 24° and 747 mm. gave 19 cc. nitrogen.

	Theory for $C_{32}H_{58}N_2S$.	Found.
N	7.73	7.84

To convert the mustard oil into dipentadecylthiourea, it was added to a calculated quantity of pentadecylamine, dissolved in alcohol, and heated for a short time. The thiourea obtained in this manner, when recrystallized from alcohol, melts at 88.5° and agrees in every respect with the dipentadecylthiourea previously prepared.

Pentadecylurea Chloride, $C_{15}H_{31}NHCOCl$.—An effort was made to obtain the urea chloride by the method employed by Gattermann[1] in preparing the lower alkyl urea chlorides.

Some pentadecylamine hydrochloride was heated in an oil-bath to 150° and a slow stream of phosgene passed over it for several hours. A small quantity of liquid was formed, which, when treated with ammonia, gave a substance melting at 109° and identified as monopentadecylurea, thus proving the liquid to be the isocyanate expected. A small amount of dipentadecylurea was also formed, but the greater portion of the amine hydrochloride remained unchanged. As the yield of isocyanate obtained by this method was very unsatisfactory, 4 grams of pentadecylamine hydrochloride and 8 cc. of liquid phosgene were heated together in a sealed tube for ten hours at 100°. On cooling, the excess of phosgene was allowed to escape and a colorless solid mass remained in the tube. This was dissolved in as small a volume as possible of benzene dried by sodium, and the small quantity of unchanged amine hydrochloride was precipitated by dry ligroin. After filtering from the hydrochloride, the benzene and ligroin were distilled while a current of dry hydrogen

[1] Ann. Chem. (Liebig), **244**, 33.

chloride was passed through the flask. A white solid remained, which, after drying on a clay plate for forty minutes in a vacuum desiccator, was analyzed and found to be pure pentadecylurea chloride formed according to:

$$C_{15}H_{31}NH_2Cl + COCl_2 = C_{15}H_{31}NHCOCl + 2HCl.$$

0.3208 gram at 752.8 mm. and 22° gave 14.5 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOCl$.	Found.
N	4.83	5.07

The urea chloride reacts readily with alcohol and amines. Whereas other urea chlorides as chlorformanilide[1] and chlorformnitranilide[2] and chlorformmethyl-[3] and ethyl amides are quite unstable, decomposing rapidly at 60°–100° into hydrochloric acid and isocyanate, chlorformpentadecylamide, is quite a stable body losing its hydrogen chloride with such difficulty that even after it was heated at 100°–150° for several hours in a stream of dry air, the hydrogen chloride had not been entirely split off. This greater stability of chlorformamides of high molecular weight is probably due to the greater basicity of the compounds on account of the increased positive character of the radical as its weight increases.

Pentadecyl Isocyanate, $C_{15}H_{31}NCO$, was prepared most readily by dissolving the urea chloride in benzene and heating it with calcium oxide, the isocyanate being liberated according to:

$$2C_{15}H_{31}NHCOCl + 2CaO = 2C_{15}H_{31}NCO + CaCl_2 + Ca(OH)_2.$$

When a test showed that the hydrogen chloride had been entirely removed, the solution was filtered from the calcium salts and the benzene distilled, the last traces being removed at reduced pressure. An oil with a slight brownish tint remained. Placed in a freezing-mixture, it solidified and then melted at 8°–14°. All precautions having been taken to prepare the cyanate in a pure condition, it was analyzed without further purification.

0.3192 gram at 745 mm. and 18° gave 15.1 cc. nitrogen.

[1] Hentschel: Ber. d. chem. Ges., 18, 1178; Lengfeld and Stieglitz: This JOURNAL, 16, 75.

[2] Swartz: This JOURNAL, 19, 311; Folin: *Ibid.*, 19, 338.

[3] Gattermann: *Loc. cit.*

	Calculated for $C_{15}H_{31}NCO$.	Found.
N	5.53	5.35

The identity of the isocyanate was confirmed by converting it, by means of aniline, into pentadecylphenylurea.

Pentadecylphenylurea, $C_{15}H_{31}NHCONHC_6H_5$. — Molecular quantities of pentadecyl isocyanate and freshly distilled aniline dissolved in benzene were heated together for a few minutes. After adding a few drops of acetic acid the benzene was distilled off, and the product recrystallized from hot alcohol. The urea melts at 94°.

0.1280 gram gave 0.1276 gram H_2O, and 0.3576 gram CO_2.

	Calculated for $C_{22}H_{38}N_2O$.	Found.
H	10.98	11.07
C	76.30	76.18

Dipentadecylurea, $(C_{15}H_{31}NH)_2CO$, was obtained in pure condition by heating together 1.1 gram (1 mol.) of pentadecyl isocyanate and 1 gram (1 mol.) of pentadecylamine and recrystallizing from alcohol.

0.3074 gram at 18° and 749.1 mm. gave 15.1 cc. nitrogen.

	Theory for $(C_{15}H_{31}NH)_2CO$.	Found.
N	5.83	5.89

The same substance was also obtained by desulphurizing the thiourea in alcohol solution with mercuric oxide.

Dipentadecylurea is difficulty soluble in hot alcohol; it crystallizes in small needles and melts at 113°.

Ethyl Pentadecylcarbamate, $C_{15}H_{31}NHCOOC_2H_5$, was prepared by boiling pentadecyl isocyanate with ethyl alcohol. It is a white crystalline body melting at 54°, and was found to be identical with the urethane obtained by a rearrangement of palmitic amide when bromine and sodium ethylate act upon it in solution in ethyl alcohol, as described below.

Pentadecyl Alcohol, $C_{15}H_{31}OH$.—Ten grams (1 mol.) of pentadecylamine hydrochloride was dissolved in alcohol and 2.6 grams (1 mol.) of sodium nitrite, dissolved in water, added to the solution. Only a small quantity of gas was generated and a white precipitate separated out. A small portion of this precipitate was filtered off and dried on a clay

plate. It was found to decompose with a rapid evolution of gas when heated to 60°. Water was then poured into the flask containing the remaining portion and the mixture boiled until gas ceased to come off. The oil, which was formed, was taken up by ether, and hydrogen chloride gas passed through the ether solution.

A white substance separated out, which was identified as unchanged pentadecylamine hydrochloride. It was found that, if the water solution is kept neutral by adding a few drops of hydrochloric acid from time to time, when necessary, the amine will all be used up in the reaction. After removing the ether by distillation, the alcohol was purified as follows: It was poured into a hot concentrated solution of calcium chloride then taken up by ether, the ether distilled and the residue boiled with water. The oil was again taken up by ether and upon removing the ether, a mixture of oil and solid remained in the flask. By dissolving the mixture in a small quantity of alcohol and placing the flask in a freezing-mixture, the oil remained in solution and the solid crystallized out.

By filtering quickly while cold, a white crystalline body melting at 45°–46° was obtained, the melting-point agreeing with that obtained by Simonini[1] for pentadecyl alcohol; the greater portion of the product was an oil, which undoubtedly consisted principally of the hydrocarbon, $C_{15}H_{30}$ (see below under undecylamine). The pentadecyl alcohol obtained was further identified by converting it into:

Pentadecyl Phenylcarbamate, $C_6H_5NHCOOC_{15}H_{31}$, which was formed when the alcohol and phenyl isocyanate were mixed together and allowed to remain in a desiccator for twelve hours. As some of the isocyanate remained unchanged, the substance was boiled with water and, in this way, the excess of isocyanate converted into diphenylurea. As diphenylurea is insoluble in ligroin, and the urethane is readily soluble, the two substances were easily separated. For analysis the urethane was recrystallized from ligroin.

0.2668 gram substance at 744.2 mm. and 19° gave 9.6 cc. nitrogen.

[1] Monatshefte, **14**, 81.

	Theory for $C_6H_4NHCOOC_{18}H_{31}$.	Found.
N	4.03	4.04

Pentadecylphenylurethane crystallizes in leaflets; it is soluble in all the organic solvents and melts at 72°. On account of its comparatively high melting-point and the ease with which it can be purified, it serves as a better means of identifying pentadecyl alcohol than any other known derivative.

The reactions studied prove conclusively that the amine obtained by distilling pentadecylurethane with slaked lime is the primary normal pentadecylamine, $C_{15}H_{31}NH_2$. In order to find whether the methods described for obtaining urethanes and amines are generally for amides of high molecular weight, the same reactions were carried out with stearic and lauric amides.

Stearic Chloramide, $C_{17}H_{35}CONHCl$, was prepared in the same manner as palmitic chloramide. As stearic amide is very difficulty soluble in cold alcohol, it is difficult to obtain the chloramide free from unchanged amide, from which it could not be separated.

0.2002 gram gave 0.0204 gram chlorine.

	Theory for $C_{17}H_{35}CONHCl$.	Found.
Cl	11.18	10.20

The analysis shows that the product obtained was not absolutely pure. No further effort was made to obtain it in pure condition, but it was further identified by converting it into the urethane, which can easily be separated from the amide by means of ligroin, in which the amide is insoluble. The urethane melts at 63°–64° and crystallizes in leaflets, and is identical with methylheptadecylurethane obtained by the direct meihod.

Methyl Heptadecylcarbamate, $C_{17}H_{35}NHCO_2CH_3$, was obtained directly from the amide by means of bromine and sodium methylate in solution in methyl alcohol, as described for preparing methylpentadecylurethane. The yield is 97 per cent of the theoretical. It was purified for analysis by recrystallization from ligroin and alcohol.

0.4584 gram substance gave 19.6 cc. nitrogen at 740.8 mm. and 20.5°.

	Calculated for $C_{17}H_{33}NHCOOCH_3$.	Found.
N	4.47	4.72

Heptadecylamine, $CH_3(CH_2)_{16}NH_2$, was prepared by distilling methylheptadecylurethane with three or four times its weight of slaked lime. Almost a quantitative yield of amine was obtained, 100 grams of amide giving about 82 grams of amine. Turpin[1] obtained only 22 grams of this amine from 100 grams of stearic amide by using aqueous alkali and bromine.

A portion of the amine dissolved in alcohol was evaporated to dryness on the water-bath with concentrated hydrochloric acid. The substance thus obtained is soluble in alcohol, insoluble in ether and decomposes at 200° without melting. It corresponds in every respect with the heptadecylamine hydrochloride obtained by Turpin.

To further identify the amine, the hydrochloride was dissolved in alcohol and evaporated to dryness on the water-bath with the molecular quantity of potassium cyanate, dissolved in water. The body obtained, when recrystallized several times from alcohol, melts at 109° and corresponds in appearance and melting-point to the monoheptadecylurea described by Turpin.

Methyl Undecylcarbamate, $C_{11}H_{23}NHCO_2CH_3$.—To 6 grams (1 equiv.) of lauric amide dissolved in 21 grams of pure methyl alcohol, and 1.4 grams (2 equiv.) of sodium dissolved in 35 grams of methyl alcohol 4.8 grams (2 equiv.) of bromine was added and the mixture boiled for about five minutes. After neutralizing the alkali with acetic acid, the alcohol was distilled and the residue was washed with water, dried, and shaken up with ligroin. A large portion remained undissolved; this was filtered off and the ligroin distilled. A white substance crystallizing in leaflets and melting at 45°–47° (near the melting-point to be expected for a methyl undecylurethane) was obtained. Although this urethane had been prepared in exactly the same manner as the other aliphatic urethanes described above, which were obtained in almost quantitative yield, it was found that, in this case, the yield was only about one-third of the theoretical. The sub-

[1] *Loc. cit.*

stance insoluble in ligroin was then examined and found to have the melting-point 102°, corresponding very closely with that of lauric amide; but when mixed with some of the pure amide, the melting-point was considerably depressed, showing it to be a different substance. This and the high melting-point indicated that the compound might be undecyllaurylurea, $C_{11}H_{23}NHCONHCOC_{11}H_{23}$, of the class of acylureas, whose formation interfered with the application of Hofmann's reaction, in aqueous solution, to higher aliphatic acid amides. This conclusion was verified as described below. For the time being, efforts were directed chiefly to obtaining a better yield of urethane.

In a second experiment the solution of sodium methylate was added in small quantities to the solution of the mixture of bromine and amide. The yield of urethane obtained was no better than before.

The third time the experiment was carried out as follows: 6 grams (1½ mol.) of bromine was added to 6 grams (1 mol.) of lauric amide dissolved in 27 grams of methyl alcohol, and a solution of 1.8 grams (2½ atoms) of sodium in 45 grams of methyl alcohol poured at once into the mixture. This time no urea was formed, but a quantitative yield of urethane was obtained. These experiments were repeated a great number of times and in every case, when the entire quantity of sodium methylate was added at once to the solution of the amide and bromine undecylurethane was obtained in excellent yield. If a portion of the solution of sodium methylate was added and but a second elapsed before the remainder was poured into the mixture, the product formed was principally urea.

To obtain the undecylurethane perfectly pure for analysis, it was dissolved in ligroin, in order to separate it from urea and unchanged amide, and then, after removing the ligroin, it was distilled at reduced pressure in an Anschütz distilling-flask.

I. 0.176 gram gave 0.4364 gram CO_2, and 0.187 gram H_2O.

II. 0.2412 gram gave 0.6008 gram CO_2, and 0.2588 gram H_2O.

III. 0.3154 gram gave 17.6 cc. nitrogen at 759.5 mm. and 19.5°.

	Calculated for $C_{11}H_{23}NHCOOCH_3$.	Found. I.	II.	III.
C	68.12	67.62	67.93	....
H	11.78	11.80	11.92	....
N	6.11	....	....	6.39

Undecylurethane is but slightly soluble in water and is much more soluble in the organic solvents than the other aliphatic urethanes obtained. It melts at 45°–47° and can be distilled at reduced pressure without decomposition.

Undecyllaurylurea, $C_{11}H_{23}NHCONHCOC_{11}H_{23}$.—The substance described above as one of the products of the reaction in the first attempt to prepare undecylurethane, was purified by recrystallization from hot ligroin. Analysis showed it to be undecyllaurylurea as expected.

0.2176 gram gave 14.2 cc. nitrogen at 744 mm. and 20°.

	Calculated for $C_{24}H_{48}N_2O_2$.	Found.
N	7.07	7.32

Undecyllaurylurea is difficultly soluble in all the organic solvents in the cold, but dissolves quite readily in hot alcohol. It crystallizes in leaflets and melts at 105°.

To identify the urea more completely it was saponified by heating it with concentrated hydrochloric acid in a sealed tube for five hours at 200°, undecylamine hydrochloride and lauric acid being formed according to :

$$C_{11}H_{23}NHCONHCOC_{11}H_{23} + 2H_2O + 2HCl = C_{11}H_{23}NH_2Cl + C_{11}H_{23}COOH + NH_4Cl + CO_2.$$

The undecylamine hydrochloride was recognized by its insolubility in ether, decomposition at 190° without melting; and by the urea obtained by treating it with potassium cyanate. The melting-point of the urea (110°) did not change when it was mixed with some of the analyzed specimen of undecylurea.

Normal Undecylamine Hydrochloride, $CH_3(CH_2)_{10}NH_2Cl$.—8 grams of methylundecylurethane were distilled with 28 grams of slaked lime. The product obtained was dissolved in alcohol, concentrated hydrochloric acid added and evaporated to dryness on the water-bath. It was purified by washing it with ether, dissolving it in a small quantity of alcohol and reprecipitating it with ether. Like the other amine hydrochlo-

rides obtained, it is insoluble in ether and decomposes without melting. It crystallizes in bright glistening plates.

I. 0.3246 gram gave 19.9 cc. of nitrogen at 741.5 mm. and 20.5°.

II. 0.2088 gram gave 0.4864 gram CO_2, and 0.2370 gram H_2O.

	Calculated for $C_{11}H_{23}NH_2Cl$.	Found. I.	II.
N	6.74	6.87	....
C	63.61	....	63.53
H	12.53	....	12.61

Undecylamine Chlorplatinate, $(C_{11}H_{23}NH_2)_2PtCl_6$, can be obtained from the amine hydrochloride by dissolving it in alcohol, adding an excess of chlorplatinic acid, and precipitating the chlorplatinate from the alcoholic solution by means of water. The chlorplatinate is a yellow crystalline body, quite soluble in alcohol and insoluble in water. It decomposes when heated to 190°.

0.4468 gram chlorplatinate gave 0.1162 gram platinum.

	Calculated for $(C_{11}H_{23}NH_2)_2PtCl_6$.	Found.
Pt	25.93	26.03

Undecylamine can be most readily identified by converting the hydrochloride into monoundecylurea. The hydrochloride, best dissolved in alcohol, and a calculated quantity of potassium cyanate, dissolved in a small quantity of water, were mixed together and evaporated to dryness. The product was thoroughly washed with water and recrystallized several times from hot alcohol. It melts at 110° and crystallizes in prismatic needles.

As the body is easily obtained in a pure condition, it serves as the most practical test for undecylamine.

0.1466 gram at 755.2 mm. and 19° gave 17 cc. of nitrogen.

	Calculated for $C_{11}H_{23}NHCONH_2$.	Found.
N	13.08	13.25

Normal Undecylamine, $CH_3(CH_2)_{10}NH_2$.—In order to obtain the free amine perfectly pure, the product obtained by distilling methylundecylurethane with lime is treated as follows: The amine is dissolved in ligroin, the solution dried with

solid potassic hydrate and filtered by the use of a siphon filter, and then further dried by heating for about two hours on the water-bath with sodium, and finally distilled over sodium.

As considerable difficulty was experienced in distilling the body on account of its foaming, it was necessary to use a much larger distilling-flask than usual. After distilling the substance from the sodium, a second distillation can be made without any difficulty. A small quantity of the body distilled at 227°–232° but the greater portion gave a constant boiling-point of 232°.

In making a nitrogen determination, it was necessary to use a very long furnace in order to keep the portion of the tube containing the substance perfectly cold, while the other end was being heated; otherwise the substance was carried over by the carbon dioxide before the tube was sufficiently hot. When cold, the substance existed as a carbonate and in that form it is not volatile.

I. 0.2508 gram substance at 749.7 mm. and 22° gave 21 cc. nitrogen.

II. 0.2642 gram substance at 744.4 mm. and 24° gave 20.6 cc. nitrogen.

	Calculated for $C_{11}H_{23}NH_2$.	Found. I.	II.[1]
N	8.18	9.31	8.56

The amine was also dissolved in alcohol and titrated with hydrochloric acid, lacmoid being used as an indicator.

I. 0.1978 gram required 11.35 cc. of $\frac{N}{10}$ hydrochloric acid.

Calculated.	Found.
11.56 cc.	11.35 cc.

0.2528 gram required 14.58 cc. $\frac{N}{10}$ hydrochloric acid.

Calculated.	Found.
14.78 cc.	14.58 cc.

At ordinary temperature undecylamine is a colorless liquid; it melts at 15° and boils at 232° under 742 mm. pressure. Like the other amines obtained, it absorbs carbon dioxide and water from the air. In the form of a carbonate it is a white solid.

[1] I was made in a short furnace and II in a long one.

An effort was made to obtain undecylamine directly by the Hofmann method, proceeding as follows: Molecular quantities of bromine and lauric amide, dissolved in a small quantity of alcohol were mixed together and poured into a hot ten per cent solution of caustic potash. A very small quantity of amine was formed, but the principal part of the product was undecyllaurylurea (m.p. 105°).

Benzoylundecylamine, $C_{11}H_{23}NHCOC_6H_5$.—The free amine gives a characteristic benzoyl derivative, which was obtained when a quantity of undecylamine (2 mols.) was dissolved in ether, and the calculated amount of benzoyl chloride (1 mol.) added. The amine hydrochloride formed was filtered, and the ether solution shaken up with a dilute caustic potash solution until no further odor of benzoyl chloride could be detected. After washing with water, the ether was distilled, and the residue dissolved in benzene and precipitated with ligroin.

0.2644 gram at 739 mm. and 20° gave 12.7 cc. of nitrogen.

	Calculated for $C_{11}H_{23}NHCOC_6H_5$.	Found.
N	5.09	5.34

Benzoylundecylamine is very soluble in alcohol, ether, and benzene, but difficultly soluble in ligroin. It crystallizes in needles and melts at 60°.

Action of Sodium Nitrite on Undecylamine Hydrochloride.

Normal undecyl alcohol being one of the few unknown primary normal alcohols, and normal undecylamine being easily prepared in quantity, as described above, it was used as a means of obtaining the alcohol. When sodium nitrite acts upon undecylamine hydrochloride secondary reactions take place, besides the usual action of nitrous acid upon the amines.

In trying the action of sodium nitrite upon primary propyl and butyl amines, V. Meyer and Fr. Forster[1] found that four products were obtained. The primary alcohol was formed in the usual manner:

$$RNH_2 + HONO = ROH + N_2 + H_2O;$$

an unsaturated hydrocarbon as follows:

[1] Ber. d. chem. Ges., 9, 529; 10, 130.

$$RCH_2CH_2NH_2 + HONO \rightarrow RCH{=}CH_2 + N_2 + 2H_2O;$$

a secondary alcohol by addition of water to the unsaturated hydrocarbon,

$$RCH{=}CH_2 + HOH \rightarrow RCHOHCH_3;$$

and a nitrosodialkylamine whose method of formation was explained by Linnemann,[1] who had previously obtained the same body by the same reaction. He assumes that amine nitrite is formed as an intermediate product, the formation of the nitrosamine then taking place according to the equation :[2]

$$2RNH_2NO_2 = R_2N.NO + N_2 + 3H_2O.$$

There is reason to believe that, when sodium nitrite acts upon undecylamine, corresponding products are formed, although but two of them were thoroughly investigated.

Normal Undecyl Alcohol, $CH_3(CH_2)_{10}OH$.—Equivalent quantities of undecylamine hydrochloride dissolved in alcohol and sodium nitrite dissolved in water, were mixed together. A white precipitate was immediately deposited, which, when filtered off and dried, was found to decompose at 60° with evolution of gas. To obtain the alcohol the amine hydrochloride and sodium nitrite in solution in water were allowed to boil gently until gas ceased to be generated, care being taken to keep the solution neutral by adding a few drops of hydrochloric acid whenever a test showed it to be alkaline.

The oil formed was taken up by ether, and the solution dried by solid potassic hydrate. After removing the ether, the oil was distilled at reduced pressure. Four fractions were collected, about one-fourth of the product boiling at 84°–90°; a small quantity at 90°–118°; about one-third at 118°–126°, and the remainder about 126°. Upon redistilling the third fraction, the greater portion of it boiled at 123°. This boiling-point is lower than that expected for an alcohol occupying such a place in the series, and analysis showed it to be still impure.

[1] Ann. Chem. (Liebig), **162**, 3.

[2] The formation of a derivative of a dialkylamine in this reaction points to the intermediate formation of a diazo body $RCH(N_2)$ which could alkylate a second molecule of the amine as easily as diazomethane methylates. The same diazo body would give with water the primary alcohol. The formation of a hydrocarbon $RCH{=}CH_2$, and particularly of a secondary alcohol, $RCHOHCH_3$, from a primary amine, points to isomeric diazo-bodies $\begin{matrix} RCH{-}CH_2 \\ | \quad | \\ N = N \end{matrix}$, whose discovery and investigation will probably be only a question of time. J. STIEGLITZ.

I. 0.3866 gram gave 1.025 gram CO_2, and 0.4440 gram H_2O.

II. 0.1928 gram gave 0.5198 gram CO_2, and 0.223 gram H_2O.

	Calculated for $C_{11}H_{23}OH$	Found. I.	II.
C	76.74	72.3	73.52
H	13.96	12.76	12.79

While the above figures are low for undecyl alcohol, yet they show that the body can be nothing but the alcohol in an impure condition. The alcohol was then further purified by converting it into undecylphenylurethane, which being a solid can be recrystallized until it gives a constant melting-point. By saponification the urethane yields the undecyl alcohol free from the hydrocarbon (see below) accompanying it, by the above method of preparation. The urethane also furnishes an excellent means of identifying the alcohol.

Normal Undecyl Phenylcarbamate, $C_6H_5NHCO_2C_{11}H_{23}$.—Six grams of the crude undecyl alcohol and 4.1 grams of phenyl isocyanate were mixed together in a flask and allowed to remain in a desiccator over night. The compound formed was dissolved in ligroin to remove any diphenylurea that might be present. After filtering, distilling off the ligroin, and recrystallizing from alcohol a number of times, a substance was obtained showing the constant melting-point 62° and crystallizing in needles.

0.2852 gram gave 12.9 cc. nitrogen at 755.7 mm. and 22°.

	Calculated for $C_6H_5NHCO_2C_{11}H_{23}$.	Found.
N	4.81	5.10

In order to convert undecylphenylurethane back into the alcohol, it was boiled for two hours with alcoholic potash. The solution was then poured into dilute acid, the oil taken up by ether, and the ether solution thoroughly washed with water, then dried for twenty-four hours with freshly-heated potassium carbonate. The alcohol remaining after removing the ether was then distilled under reduced pressure. The body when purified as described boiled at 131°, at 15° mm. pressure, and melted at 19°. Although both boiling-point

and melting-point are those expected for undecyl alcohol, the figures obtained in analyzing the body were still a little low, showing a slight impurity.

0.2466 gram gave 0.6828 gram CO_2, and 0.2964 gram H_2O.

	Calculated for $C_{11}H_{23}OH$.	Found.
C	76.74	75.51
H	13.95	13.35

In order to determine whether the alcohol obtained was the primary or secondary (see above), it was oxidized by taking one part of the alcohol, two of potassium bichromate, three of sulphuric acid and nine of water, and boiling the mixture gently under an inverted condenser for twenty hours. The resulting product was extracted with ether, and the ether extract washed with water. After removing the ether by distillation, the residue was dissolved in alcohol and when the flask containing the solution was placed in a freezing-mixture, white crystals were formed. The crystals were filtered in a funnel surrounded by a freezing-mixture. The body had an acid reaction, and melted at 26°.

The silver salt was prepared by suspending the acid in water, neutralizing with ammonia and adding an excess of silver nitrate. The salt was washed, first with water, then with a small quantity of alcohol.

0.1602 gram gave 0.0577 gram silver.

	Calculated for $C_{11}H_{21}O_2Ag$.	Found.
Ag	36.86	36.01

The analysis of the silver salt, as well as the melting-point (26°), shows the oxidation product to be normal undecylic acid (m. p. 28.5°); consequently the substance from which it was obtained, must have been the hitherto unknown primary normal undecyl alcohol.

Undecylene, $CH_2(CH_2)_8CH : CH_2$.—The fraction boiling below 90°, which was obtained by distilling the product formed by the action of sodium nitrite on undecylamine hydrochloride, was redistilled. The greater portion of the product boiled at 84° at 18 mm. pressure.

0.1754 gram gave 0.5394 gram CO_2, and 0.225 gram H_2O.

	Calculated for $C_{11}H_{23}$.	Found.
C	85.71	83.86
H	14.28	14.25

As the analysis showed that the substance was not quite pure, it was converted into the dibromide, the boiling-point of which is so much higher than that of any of the other products that might be present, that there could be no difficulty in separating it from them by distillation.

Undecylene Dibromide, $CH_3(CH_2)_8CHBrCH_2Br$.—The undecylene (b.p. 84°, 18 mm.) was cooled in a freezing-mixture, and the calculated amount of bromine diluted by three and a half times its volume of carbon disulphide, added drop by drop. After removing the carbon disulphide, the heavy oil was distilled at reduced pressure. At 18 mm. it showed the constant boiling-point 161°.

A bromine determination by the Carius method gave the following results:

0.2068 gram substance gave 0.2490 gram AgBr.

	Calculated for $C_{11}H_{22}Br_2$.	Found.
Br	50.95	51.23

Nothing further was done with the second and fourth fractions excepting that a test showed the fourth fraction to be rich in nitrogen, the principal object of the study of the reaction being to determine whether the method could be used for preparing undecyl alcohol. Although undecyl alcohol is formed according to the equation,

$$C_{11}H_{23}NH_2Cl + NaONO = C_{11}H_{23}OH + N_2 + NaCl + H_2O,$$

the method is not to be recommended, as the yield obtained is very small, and it is very difficult to separate the alcohol from the other products of the reaction.

Preparation of Urethanes Directly from Acid Amides Dissolved in Ethyl Alcohol.

The yield of urethanes obtained by treating an acid amide dissolved in ethyl alcohol with sodium ethylate and bromine, is somewhat lower than that obtained when methyl alcohol is used as the solvent, yet, in every case in which the method has been tried, it is much higher than that obtained by the older method.

Ethyl Phenylcarbamate, $C_6H_5NHCO_2C_2H_5$.—The yield of ethylphenylurethane obtained by Swartz by treating dry benzbromamide with sodium ethylate was only 15 per cent of the theoretical, the remainder of the product being phenylbenzoylurea and unchanged amide. By proceeding in the following manner, a yield corresponding to 70 per cent of the theoretical was obtained.

5.7 grams (3 atoms) of sodium were dissolved in 142 grams of ethyl alcohol and the solution poured into a mixture of 10 grams (1 mol.) of benzamide, dissolved in 85 grams of ethyl alcohol, and 19 grams (1½ mols.) of bromine. The mixture was boiled for a few minutes on the water-bath, the alcohol distilled and the residue washed with water. After the product was thoroughly dried on a clay plate, it was distilled at reduced pressure. 9.6 grams of pure ethylphenylurethane were obtained, melting at 52°.

Ethyl-m-Nitrophenylcarbamate, *m*-$NO_2C_6H_4NHCO_2C_2H_5$.—By the older method Swartz obtained 6 per cent of ethyl-*m*-nitrophenylurethane and 53 per cent of nitrobenzoylphenylurea. By proceeding as in the last case 56 per cent of urethane was obtained with a considerable quantity of unchanged amide, but no urea.

Ethyl Pentadecylcarbamate, $C_{15}H_{31}NHCO_2C_2H_5$.—2.7 grams (3 atoms) of sodium, dissolved in 65 grams of ethyl alcohol, were poured into a mixture of 9.3 grams (1½ mols.) of bromine and 10 grams (1 mol.) of palmitic amide, dissolved in 40 grams of ethyl alcohol. After heating the mixture for a few minutes on the water-bath, a few drops of acetic acid were added and the alcohol distilled. The residue was washed with water, dissolved in ligroin and the undissolved portion filtered off. After removing the ligroin, the substance was distilled at 14 mm. pressure. It boils at 225° (14 mm.), and melts at 54°. It corresponds in every respect with the urethane obtained by me synthetically. The yield is 50 per cent of the calculated.

0.4838 gram at 749.5 mm. and 16° gave 21 cc. nitrogen.

	Calculated for $C_{15}H_{31}NHCOOC_2H_5$.	Found.
N	4.68	4.99

As in so many cases ureas were formed with such remarkable ease in the presence of alcohol (see undecyllaurylurea), some experiments were tried in order to find out whether they could be obtained by the direct action of an isocyanate upon an amide in alcoholic solution.

1. To a mixture of 1 gram (1 mol.) of benzamide, dissolved in 8 grams of methyl alcohol, 1 gram (1 mol.) of phenyl isocyanate was added, and the mixture heated for about five minutes on the water-bath. The products obtained, when purified, were identified as unchanged amide and phenylmethylurethane.

2. To 1 gram of benzamide in a 10 per cent caustic potash solution, 1 gram of phenyl isocyanate was added, and the mixture shaken up until the odor of isocyanate disappeared. The products obtained were diphenylurea (m. p. 235°) and unchanged amide.

3. 1.3 grams (1 mol.) of phenylurea chloride was added to 1 gram (1 mol.) of benzamide, dissolved in 12 grams of methyl alcohol, and the mixture heated for a few minutes on the water-bath. The odor of benzoic ether was quite noticeable, the other products obtained being ammonium chloride and phenylmethylurethane.

4. To a mixture of 1 gram (1 mol.) of benzamide, dissolved in 4 grams of methyl alcohol and 0.3 gram of sodium dissolved in 8 grams of methyl alcohol, 1.3 grams (1 mol.) of phenylurea chloride were added. The products obtained were benzamide and methylphenylurethane.

As not the slightest trace of phenylbenzoylurea was obtained in any of the above experiments, it is quite evident that an isocyanate, in its ordinary condition, does not act upon an amide as readily as upon an alcohol.

Action of Sodium Methylate and Bromine on Cinnamic Amide.

To a mixture of 8 grams of cinnamic amide dissolved in 45 grams of methyl alcohol, and 2.7 grams (2 atoms) of sodium, dissolved in 70 grams of methyl alcohol, 8.7 grams of bromine were added in small portions at a time. The mixture was heated for a short time on the water-bath, and after adding a

few drops of acetic acid, the alcohol was allowed to evaporate spontaneously. The product remaining was shaken up with ether. A portion dissolved, but a considerable quantity remained undissolved. The undissolved portion was washed with water to remove the sodium bromide, and for analysis it was recrystallized two or three times from alcohol. The body melts at 218° with decomposition.

I. 0.1566 gram gave 7.5 cc. nitrogen at 747.5 mm. and 16°.

II. 0.1402 gram gave 0.2358 gram of CO_2, and 0.0618 gram H_2O.

	Calculated for $C_{10}H_{12}NO_2Br$.	Found.
C	46.51	45.86
H	4.65	4.89
N	5.42	5.49

The presence of considerable bromine in the compound was proved by a qualitative test. No rearrangement had taken place, as the body, when heated with a solution of caustic potash, gave off ammonia, showing that the amido group had remained unchanged. No effort was made to determine the constitution of the body, but in all probability the constitutional formula is $C_6H_4CHBrCH(OCH_3)CONH_2$, or possibly with the bromine and methoxy group exchanged.

From the ether solution a thick pasty substance was obtained which could not, by any means employed, be crystallized, and as it decomposed when distilled *in vacuo*, it was not obtained sufficiently pure for analysis.

Action of Sodium Methylate and Bromine upon Salicylic Amide.

McCoy[1] in treating salicylic amide with bromine and alkali in solution in water according to Hofmann's reaction, found that the benzene ring is brominated twice before the rearrangement is effected. The same reaction when tried by me in methyl alcohol, gave the same result. The experiment was carried out as follows:

To a mixture of 10 grams (1 mol.) of salicylic amide, dissolved in 66 grams of methyl alcohol and 5 grams (3 atoms) of sodium, dissolved in 110 grams of methyl alcohol, 11.6 grams (1 mol.) of bromine were added. The product obtained was identified as dibromsalicylic amide melting at 183°.

[1] This JOURNAL, **21**, 116.

It is evident that the method of preparing urethanes, described in this paper, cannot on account of the reactivity of the reagents, be used to effect a rearrangement of bodies analogous to salicylic or cinnamic amide. In such cases the method of Curtius[1] is the most satisfactory.

The results of the work described in this paper and the conclusions to be drawn from them can be briefly summarized as follows:

1. Urethanes are obtained without the isolation of the brom- or chloramides by the action of a sodium alcoholate on a mixture of an acid amide and bromine.

The method is applicable to the preparation of both aromatic and aliphatic urethanes, in ethyl and methyl alcohol solution, but cannot be used when the acid amide is unsaturated or otherwise very susceptible to bromine.

2. The urethanes, when distilled with slaked lime, give amines quantitatively according to

$$RNHCOOCH_3 + Ca(OH)_2 = RNH_2 + CaCO_3 + HOCH_3.$$

As the urethanes were also obtained in excellent yield, this method was found to be a practical one for the preparation of higher aliphatic amines.

3. The amines, obtained by the above-described method, are primary monoalkylamines as shown: (*a*) by the preparation of a mustard oil and an isocyanate from pentadecylamine; (*b*) by the formation of primary alcohols when sodium nitrite was allowed to act upon the amine hydrochlorides.

4. The formation of acyl alkylureas in applying the Hofmann reaction in aqueous or alcoholic solution takes place whenever, owing to the slowness of the reaction, considerable unchanged acid amide is present, while the remainder of the acid amide is suffering "rearrangement"; the rearranged portion then acts upon the unchanged amide even in the presence of alcohol or water and forms a urea.

5. Experiments show that an isocyanate in its ordinary condition, will not act upon an acid amide in the presence of alcohol or water.

I wish here to express my sincere thanks to Professor Stieglitz, who directed and advised me in this work.

[1] J. prakt. Chem., **52**, 227, 433.

Contributions from the Chemical Laboratory of Harvard College.

CXIII.—AN ELECTRIC DRYING OVEN.

By Theodore William Richards.

Practical chemists have long sought for an ideal drying oven. The qualities which should be possessed by this piece of apparatus are the following: cleanliness, durability, ease of regulation, constancy, and cheapness. Porcelain and glass are the only materials, except platinum, which commend themselves to the accurate experimenter as far as cleanliness is concerned; but these substances are so easily cracked by rapidly changing temperature that some ignoble metal is usually chosen, with the well-known untidy results. If illuminating gas is used as the source of heat, the products of combustion should be carefully excluded from the interior of the oven, because of the sulphurous oxide which is present; hence a large part of the heat is usually wasted.

The commercial use of electricity as a heating agent is well known to all, and the difficulties referred to above can be so readily overcome by its assistance, that an electric drying oven for chemists cannot be a new thing. Nevertheless, since such a piece of apparatus is not commonly known, perhaps the hints contained in this brief note may be useful to those who have not happened to think of the device.

An ordinary sixteen candle-power incandescent lamp gives heat enough to raise a small oven padded with asbestos to 120° or 130°. It may be arranged in the fashion sketched in the first figure, a large lamp-chimney serving as the lining of the oven, while the outside casing consists of a "tin" can with holes cut in the bottom and the lid. The crucible or funnel to be heated may be supported either from above or from below.

While simple contrivances of this kind may occasionally answer, the brilliant light shed by this source of heat is not permissible when some substances are to be dried; and, moreover, larger vessels must often be heated, and higher temperatures attained.

Obviously a great variety of resistances might be used for

converting the electrical energy into heat, and with alternating currents ohmic resistance might be assisted by impedance and hysteresis. By suitable adjustment of current and other circumstances, any temperature between the temperature of the room and 3000° or more might be obtained; but the present description is concerned only with the easily obtained conditions necessary to operate a drying oven suited to the uses of the analytical chemist.

A coil of wire wrapped around a suitable insulator is perhaps the most convenient resistance for the present purpose, and while iron or German silver wire will serve for a short time, platinum is of course the best material. A platinum wire 0.2 mm. in diameter, exposed to warm air, is heated almost but not quite to redness by a current of two amperes; and, since two amperes may be safely taken from a circuit designed for electric lighting, this wire is a convenient size. Five meters of this wire, when thus heated, have a resistance of not far from twenty-five ohms,—the resistance needed if one has a fifty volt current at his disposal. The corresponding amount of energy (100 watts, or twice the amount taken by a sixteen candle-power lamp) is capable of heating an oven large enough for most of the needs of an analytical chemist. The form and thermal insulation of the oven have so much effect upon the result that the details must be largely a matter of trial; but these figures will enable anyone who has a slight knowledge of electricity to arrange a contrivance approximately suited to his own needs. For example, from the common 8 volt accumulator plant one must draw five or six amperes for a small oven, and two or three times that amount for a large one; a thin ribbon of platinum foil would probably form the best resistance with this large current. The oven should of course be adjusted to furnish the maximum temperature desired; for diminution of the current by the interposition of outside resistance, or admission of more air, enables one to lower this temperature to any degree.

The most serious difficulty which was encountered in the practical execution of the plan was the inequality of the temperatures observed in different parts of the bath, an inequality which may easily amount to as much as 30° or 40°. This

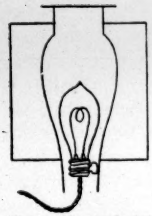


Fig. 1. Simple drying oven using an incandescent lamp as the source of heat.

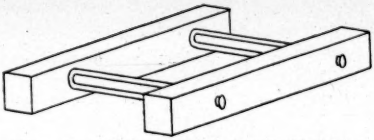


Fig. 2. Frame of porcelain and glass around which a platinum resistance may be wound.

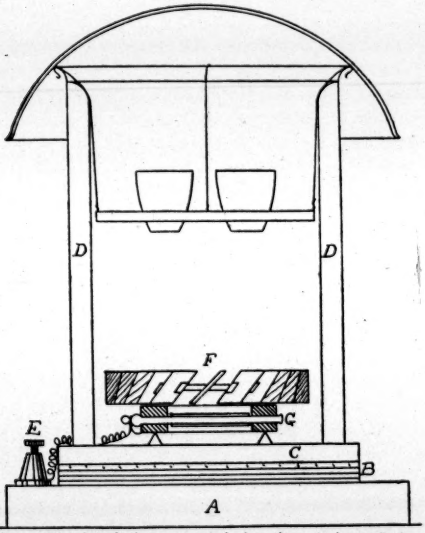


Fig. 3. Complete drying oven, vertical section. A=base; B=layers of asbestos to protect base; C=porcelain tile; D=annular space packed with non-conducting material; E=wire leading to resistance; F=stationary fan made of inclined mica vanes attached to platinum foil; G=section of frame shown in Fig. 2.

difficulty may be completely overcome by a stationary propeller-diaphragm placed directly over the coil of heated wire. The oblique vanes of this diaphragm produce a spirally ascending current which causes the air in the oven to mix in a very thorough manner, so that a thermometer near the walls gives a temperature within 2° of that registered by a thermometer in the center.

A brief description of the general problem having been given, the details of a simple but efficient air-bath built in accordance with these principles may not be out of place.

The base of the oven consists of a stout piece of hard wood 20 cm. square [A, Fig. 3.]. Upon it rest several alternate squares of ignited asbestos paper and wire gauze [B], and upon these rests a porcelain tile [C], which forms the bottom of the chamber. The walls of the oven are formed by a large beaker, 12 cm. in diameter, cut off horizontally near its base, and 20 cm. high. The annular space [D] between this beaker and a larger one encircling it, is partially filled with three or four layers of ignited asbestos paper, or with loosely packed asbestos wool, in order to prevent loss of heat. A large "clock" glass or, if darkness is needed, an inverted evaporating dish or a porcelain tile, forms the lid, which also should be provided with an asbestos covering. When access to the interior is desired the whole cylindrical wall may be raised, or merely the lid removed, according to the needs of the occasion.

Two binding-posts, screwed into the wood, serve to connect the apparatus with the source of energy (52 volts). Medium-sized platinum wires [E] lead the current beneath the broken edges of the beaker to the heat-producing resistance, which may be mounted in the base of the chamber upon one of a variety of insulators of porcelain, glass, or mica. A very convenient arrangement for this purpose consists of two of the ordinary porcelain clamps (8 cm. long) used for securing electric wires, held together by glass rods passed through their screw holes, and held apart by shorter glass tubes encircling the rods. Around the porcelain sides of this frame (which is shown in Fig. 2) are tightly wound the 5 meters of No. 32 (B. & S.) platinum wire (0.2 mm. in diameter and 3.4 grams

in weight) the coils being laid at least 1.5 mm. apart to avoid accidental contact when the wire expands upon heating. In some cases plates of mica have been used to prevent this contact, but usually this precaution is unnecessary. The frame, with its resistance-wire, is supported half a centimeter above the base by means of pieces of pipe-stem or of glass; and above this, propped upon other bits of pipe-stem, or upon a glass stand, is placed the stationary screw-propeller [F] which agitates the ascending column of air. Obviously nothing is easier than to regulate the amount of air admitted by raising or lowering the cylindrical wall. The screw propeller may be made by simply cutting radial slits in a disk of tinned iron or platinum foil, and turning the segments to an angle of 45° with the plane of the disk; or it may be made of mica vanes attached to a platinum center, according to the purse and the taste of the user. The tinned iron disc will probably answer most purposes, for it is readily replaced when worn out.

The vessel to be heated may be supported by a tripod from below, or perhaps more neatly by a triangle or quadrangle suspended from above. By the judicious combination of pipe-stem or glass tube and platinum wire, a support may be made which is both strong and inexpensive. If platinum alone is used the wire must be stout and therefore costly. This oven gives a temperature 140° above that of the room in which it is placed, when no outside resistance is interposed.

It is needless to point out the great cleanliness, convenience, safety, and economy of this simple drying apparatus. The real test of such a device is to be found in its daily performance, and this is so satisfactory in constancy and in ease of accurate regulation at any desired point as to leave nothing to be desired. Large ovens for the use of classes have not yet been constructed, but probably no difficulty will be experienced in building permanent structures which will be a boon to students in quantitative analysis.

CXIV.—ON CERTAIN DERIVATIVES OF SYMMETRICAL TRICHLORBENZOL.[1]

By C. Loring Jackson and F. H. Gazzolo.

In a paper by Sidney Calvert and one of us,[2] the behavior of tribromiodbenzol, $Br_3I_1,3,5,I_2$, and of tetrabrombenzol, $Br_4I_1,2,3,5$, with sodic ethylate was studied, and it was shown that the atom of iodine (or the atom of bromine in the corresponding position) was replaced by hydrogen under these conditions, giving the symmetrical tribrombenzol. It seemed of interest in this connection to study the corresponding trichlor compounds; that is, the trichloriodbenzol and the trichlorbrombenzol, to see whether the loosening effect of the three chlorine atoms might not be even greater than that of the three atoms of bromine, and thus make it possible that these substances would react with other agents besides sodic alcoholates, which were the only reagents that had any such effect upon the bromine compounds.

At that time it was not worth while to undertake the work, because of the great difficulty in preparing symmetrical trichloraniline, but since this obstacle has been removed by the beautiful method of Victor Meyer and Sudborough,[3] we have prepared these compounds and studied some of their relations. Trichloriodbenzol, $Cl_3I_1,3,5,I_2$, melts at 55°; and by treatment with sodic ethylate dissolved in alcohol and benzol, yielded symmetrical trichlorbenzol recognized by its melting-point 64° and two analyses. It therefore behaved like the tribromiodbenzol under these conditions. All our other attempts to obtain a simple replacement of the iodine in this substance failed, so that it is no more reactive than the tribromiodbenzol. Fuming nitric acid converted the trichloriodbenzol into the trichlordinitrobenzol melting at 129°, iodine being set free.

The trichlorbrombenzol, $Cl_3I_1,3,5,Br_2$, melts at 65°; that is, at nearly the same temperature as the symmetrical trichlorbenzol 63°.4 (Körner), and what is strange, higher than the

[1] Presented to the American Academy of Arts and Sciences, October 12, 1898.

[2] This Journal, **18**, 298.

[3] Ber. d. chem. Ges., **27**, 3151.

corresponding trichloriodbenzol. With sodic ethylate it lost bromine, but the reaction was not specially studied. When treated with fuming nitric acid it gave a trichlorbromdinitrobenzol melting at 175°, which was a decidedly reactive substance. Aniline replaced the three atoms of chlorine, giving the trianilidobromdinitrobenzol, $C_6(C_6H_5NH)_3Br(NO_2)_2$, melting at 175°–176°, discovered by W. D. Bancroft and one of us.[1]

Sodic ethylate also acts upon it, probably giving a number of products, to judge from analogy and the fact that both sodic bromide and sodic nitrite were detected among them, but we have only succeeded in identifying one of these with certainty; this is a bromdinitroresorcine diethylether melting at 81°–82°, and probably having the following constitution, $(OC_2H_5)_2$1,3,Br2$(NO_2)_2$4,6, although it may be that one of the ethoxy groups stands at 5 instead of 3. It must have been formed by the replacement of two atoms of chlorine by two ethoxy groups, and the third by hydrogen. As in most of the replacements of a halogen by hydrogen it has been found that it stood between two nitro groups, we think there can be little doubt that the first constitution assigned to this body is the correct one. Its formation is interesting, as it is the first case we have found in which chlorine has been replaced by hydrogen under these conditions. In all the other cases studied the chlorine has remained unaltered or has entered into some simple reaction: thus picryl chloride gave picryl ether,[2] picryl malonic ester,[3] or picryl acetacetic ester,[4] according to the reagent used; chloranil gave dichlorquinonedimalonic ester;[5] or, so far as the replacement alone was concerned, dichlordiethoxyquinone,[6] and trichlordinitrobenzol gave dichlordinitrophenylmalonic ester,[7] or chlordinitroresorcine diethylether, and dinitrophloroglucine triethylether.[8] These last cases are especially striking, since the corresponding tribromdinitrobenzol showed a replacement of bromine by hydrogen, when treated with sodium malonic ester or sodic ethylate.

[1] This JOURNAL, **12**, 294.
[2] Jackson and Boos: *Ibid.*, **20**, 444.
[3] Jackson and Soch: *Ibid.*, **18**, 133.
[4] Dittrich: Ber. d. chem. Ges., **23**, 2720.
[5] Stieglitz: This JOURNAL, **13**, 38.
[6] Kehrmann: J. prakt. Chem. [2], **40**, 367; Jackson and Grindley: This JOURNAL, **17**, 602.
[7] Jackson and Lamar: This JOURNAL, **18**, 775.
[8] Jackson and Lamar: *Ibid.*, p. 668.

This bromdinitroresorcine diethylether, melting at 81°-82°,

$$(OC_2H_5)_2,1,3,Br2,(NO_2)_2,4,6?$$

is isomeric with that melting at 184°,

$$(OC_2H_5)_2,1,5,Br3,(NO_2)_2,2,4,$$

and that melting at 92°,

$$(OC_2H_5)_2,1,3,Br5,(NO_2)_2,2,4,$$

made by the action of sodic ethylate on the symmetrical tribromdinitrobenzol.

The trichlorbromdinitrobenzol also reacted with sodium malonic ester, but we were unable to bring the product into a state fit for analysis. When the dry substance was treated with sodic ethylate, it gave a deep vermilion product, which probably belongs to the class of colored compounds formed by sodic ethylate and certain nitro bodies,[1] as it was decomposed by water and some organic solvents. This is the first case, so far as we can find, in which one of these substances has been observed derived from a compound of benzol with all its atoms of hydrogen replaced by other radicals.

Trichloriodbenzol, $C_6H_2Cl_3I$.

To prepare this substance 17 grams of sublimed trichloraniline (made by the excellent method of V. Meyer and Sudborough[2]) were mixed with moderately dilute sulphuric acid in the proportion of 1 molecule of trichloraniline to each molecule of sulphuric acid, and after thorough cooling powdered sodic nitrite was added in small successive quantities, until the nitrous fumes generated were no longer absorbed. After each addition of the sodic nitrite the flask was corked and vigorously shaken, until all the red fumes were absorbed, care being taken that the contents were kept cool throughout the operation. When a sufficient amount of sodic nitrite had been added, the mixture was filtered, the cooled filtrate freed as completely as possible from the excess of nitrous fumes by vigorous shaking, and then treated with a distilled aqueous solution of hydriodic acid, until there was no further action.

[1] This JOURNAL, 19, 199, where a complete list of the papers on this subject is given.

[2] Ber. d. chem. Ges., 27, 3151.

The brownish precipitate thus obtained was washed, first with a solution of potassic iodide to remove free iodine, and finally with water, after which it was purified by sublimation, or by crystallization from hot alcohol, until it showed the constant melting-point 55°. It was dried *in vacuo*, and gave the following results on analysis:

0.2188 gram of the substance gave, by the method of Carius, 0.4746 gram of a mixture of argentic chloride and iodide. After washing this precipitate with ammonic hydrate, 0.1672 gram of argentic iodide was left undissolved.

	Calculated for $C_6H_3Cl_2I$.	Found.
Cl and I	75.94	76.10
Cl	34.69	34.73
I	41.30	41.29

The substance is therefore trichloriodbenzol, and as it was made from ordinary trichloraniline its constitution must be $Cl_1,I_3,5,I_2$.

Properties of Trichloriodbenzol.—It crystallizes from alcohol in white, slender needles terminated by one plane at a very acute angle; these needles are often a centimeter or more long, and are much branched, the branches forming a sharp angle with each other and developing into forms like feathers. It melts at 55° and sublimes easily. It is freely soluble in ether, benzol, chloroform, acetone, carbonic disulphide, or ligroin; soluble in ethyl or methyl alcohol, when cold, more freely soluble when hot; soluble in glacial acetic acid; insoluble in water, cold or hot. A mixture of alcohol and chloroform is the best solvent for it. It is apparently unaffected by the strong acids, or by sodic, potassic, or ammonic hydrate.

Behavior of Trichloriodbenzol with Sodic Ethylate.

Two grams of trichloriodbenzol dissolved in anhydrous benzol were mixed with 20 cc. of an alcoholic solution of sodic ethylate made from 1 gram of sodium, and the mixture was allowed to stand over night. The liquid turned dark brown, and a precipitate began to separate soon after adding the ethylate. To make certain that the reaction was complete, the mixture was heated on the steam-bath in a flask with a return condenser, which rendered the brown color much

darker. The product was then evaporated to dryness. During the evaporation an odor like that of an aldehyde was observed, but the presence of one could not be determined by other tests. The dry residue was treated with water, and the insoluble portion separated from the solution, which gave tests for an iodide. The portion insoluble in water, which was very dark brown, was washed thoroughly, and then purified by crystallization from alcohol, until it showed the constant melting-point, 64°, which proved that it was the symmetrical trichlorbenzol. This was confirmed by the following analyses of the substance dried *in vacuo*:

I. 0.0906 gram of the substance gave, by the method of Carius, 0.2154 gram of argentic chloride.

II. 0.0792 gram of the substance gave 0.1862 gram of argentic chloride.

	Calculated for $C_6H_3Cl_3$.	Found. I.	II.
Cl	58.68	58.78	58.13

Behavior of Trichloriodbenzol with Other Reagents.

With aniline even at its boiling-point trichloriodbenzol showed no signs of action, except that the color of the mixture became darker, and a certain amount of turbidity appeared, but no test for an iodide could be obtained, and the trichloriodbenzol was recovered unaltered.

When trichloriodbenzol was heated on the steam-bath for three hours with an aqueous solution of sodic hydrate, the liquid took on a chrome-yellow color, but this must have been due to a very slight reaction, as after acidification it gave no precipitate with argentic nitrate, and essentially the whole of the trichloriodbenzol was recovered unaltered.

Melted sodic hydrate, on the other hand, seemed to act upon it, as a brownish mass was obtained, which after solution in water gave a slight precipitate on acidification and a reddish solution; a good test for an iodide was obtained, but the yield of the new organic substance was so small that we did not study this reaction further, since at best it seemed to us of slight interest.

Sodium malonic ester had little or no action on the trichloriodbenzol, most of which was recovered unaltered from the

product, so that the hope of obtaining enough of a substance (if one were really formed) for analysis was so small that we did not continue work in this line.

From these experiments it appears that the trichloriodbenzol is no more reactive than the tribromiodbenzol, from which exactly similar results were obtained by Sidney Calvert and one of us.[1]

When trichloriodbenzol was mixed with nitric acid of specific gravity 1.50 and strong sulphuric acid, and the mixture gently heated, the solid went into solution. It was allowed to stand at the ordinary temperature over night, and then precipitated with a large quantity of water, when a mixture of a white body and scales of iodine was thrown down. The iodine was recognized by its crystalline form, color, smell, and purple fumes. The white body was purified by crystallization from alcohol, when it showed the melting-point 129°, and is therefore the trichlordinitrobenzol, Cl_3, 1, 3, 5, $(NO_2)_2$, 2, 4.

Trichlorbrombenzol, $C_6H_2Cl_3Br$.

Twenty grams of trichloraniline dissolved in 100 cc. of hot glacial acetic acid were mixed with 90 cc. of hydrobromic acid (boiling at 125°), and, disregarding the heavy, grayish-yellow precipitate, the mixture was thoroughly cooled in an ice-bath, and then treated with powdered sodic nitrite, until red fumes were given off freely. The sodic nitrite was added in small quantities at a time, and the flask containing the mixture shaken vigorously after each addition, the liquid being kept cool throughout. The heavy precipitate already mentioned went into solution during the addition of the sodic nitrite, forming a dirty yellow liquid. After standing for a few hours to complete the reaction, the contents of the flask were poured into an evaporating-dish, and heated for an hour on the steam-bath. In this way a dark oily product floating on the surface of the liquid was obtained, which solidified on cooling. The mother-liquor deposited more of this product in a semicrystalline condition, and an additional amount was obtained from it by heating it again with more hydrobromic acid. The product was purified by sublimation, followed by

[1] This JOURNAL, 18, 304.

recrystallization from alcohol, until it showed the constant melting-point, 64°–65°. As this is the same as the melting-point of trichlorbenzol, we supposed at first that our product was this body, but the following analyses of the substance dried *in vacuo* showed that it was the desired trichlorbrombenzol.

I. 0.1618 gram of the substance gave, by the method of Carius, 0.3850 gram of the mixture of argentic chloride and bromide.

II. 0.1116 gram of the substance gave 0.2656 gram of the mixture of argentic chloride and bromide.

III. 0.1276 gram of the substance gave on combustion 0.1274 gram of carbonic dioxide and 0.0108 gram of water.

	Calculated for $C_6H_2Cl_3Br$.	Found. I.	II.	III.
Cl and Br[1]	71.60	71.76	71.74	....
C	27.64	....	....	27.23
H	0.77	....	....	0.94

The yield of trichlorbrombenzol was 12 grams, instead of the 26.5 grams which should have been obtained from 20 grams of trichloraniline, that is, over 45 per cent of the calculated quantity.

Properties of Trichlorbrombenzol.—It crystallizes from alcohol in white radiating needles, which develop into long, slender, blunt-ended prisms. It melts at 64°–65°; that is, one degree higher than the symmetrical trichlorbenzol, which melts, according to Körner, at 63°.4; not only is this coincidence striking, but it is also surprising that it should melt at a higher temperature than the trichloriodbenzol, which melts at 55°. It sublimes easily. It is freely soluble in ether, benzol, or acetone; soluble in cold alcohol, more freely in hot; soluble in glacial acetic acid, or ligroin; less soluble in methyl alcohol, and still less in carbonic disulphide. The best solvent for it is alcohol. The three strong acids have no apparent action on it, but fuming nitric acid converts it into trichlorbromdinitrobenzol, as described later. When a benzol solution of the trichlorbrombenzol was treated with sodic

[1] By a curious coincidence the results of analyses I and II, if calculated as argentic chloride, give numbers agreeing excellently with the percentages calculated for $C_6H_3Cl_3$, so that the combustion was necessary to determine whether our compound was this, or the $C_6H_2Cl_3Br$, which has the same melting-point.

ethylate, the atom of bromine was removed, as was shown by testing the wash-waters from the product for bromine, when a strong reaction for it was observed.

Trichlorbromdinitrobenzol, $C_6Cl_3Br(NO_2)_2$.

To prepare this substance the trichlorbrombenzol was mixed with nitric acid of specific gravity 1.52, and one-third the quantity of strong sulphuric acid, and the mixture heated gently for an hour. At first the solid dissolved, but later the nitro compound was deposited from the solution. After the mixture had stood over night, the supernatant acid was poured into a large quantity of water, which gave an additional amount of the product. It was purified by crystallization from a mixture of alcohol and benzol until it showed the constant melting-point, 175°, when it was dried *in vacuo*, and analyzed with the following result:

0.1654 gram of the substance gave, according to the method of Carius, 0.2914 gram of the mixture of argentic chloride and bromide.

	Calculated for $C_6Cl_3Br(NO_2)_2$.	Found.
Br and Cl	53.21	53.10

The constitution of this substance is settled by the method by which it was made as Cl,1,3,5,Br2,(NO_2),4,6. The yield is essentially quantitative.

Properties of Trichlorbromdinitrobenzol.—It forms, when crystallized from alcohol and benzol, thick, rather blunt, rhombic plates, the obtuse angles of which are frequently beveled by two planes. They show a tendency to form groups with the members superimposed, and have a slight yellowish tinge. The substance melts at 175°, and is very soluble in chloroform, acetone, or carbonic disulphide; slightly soluble in ethyl or methyl alcohol, either cold or hot; insoluble in cold, soluble in hot glacial acetic acid; essentially insoluble in ligroin, or in hot or cold water. The best solvent for it is a mixture of benzol and alcohol. Strong hydrochloric or sulphuric acid has no apparent action on it. Fuming nitric acid dissolves it when hot. It sublimes easily, and in this way feathery, ivory-white crystals are obtained sometimes over a centimeter in length.

Action of Aniline on Trichlorbromdinitrobenzol.

When one gram of trichlorbromdinitrobenzol was warmed gently with a slight excess of freshly-distilled aniline it went into solution, forming a cherry-red liquid, the color of which became deeper on longer heating. To obtain the product the liquid was poured into a large quantity of water, acidified with hydrochloric acid, and the crimson precipitate formed in this way thoroughly washed and crystallized from a mixture of alcohol and benzol until it reached the constant melting-point, 175°–176°. This showed that the substance was the bromdinitrotrianilidobenzol, $C_6Br(NO_2)_2(C_6H_5NH)_3$, obtained by W. D. Bancroft and one of us[1] from tetrabromdinitrobenzol and aniline. In this case it was formed by the replacement of the three atoms of chlorine by three anilido groups.

Behavior of Trichlorbromdinitrobenzol with Sodic Ethylate in the Cold.

Five grams of trichlorbromdinitrobenzol dissolved in anhydrous benzol were mixed with the sodic ethylate made from 25 grams of absolute alcohol and 1 gram of sodium, which gave the proportion of 3 molecules of the ethylate to each molecule of trichlorbromdinitrobenzol. The two substances reacted at once, since the liquid took on a bright scarlet color as soon as they were mixed, and there was also a slight evolution of heat. To complete the reaction the mixture was allowed to stand three days at ordinary temperatures, during which time a heavy precipitate was deposited, and the color changed to a yellowish-red. The precipitate was filtered out, washed with alcohol, and then dissolved in water. This solution gave a strong test for sodic nitrite with potassic iodide, starch paste, and dilute sulphuric acid, and also a heavy white precipitate with argentic nitrate and nitric acid. To obtain the organic products of the reaction the reddish alcoholic filtrate was allowed to evaporate spontaneously, and the residue treated with water; the insoluble substance thus obtained was purified by crystallization from alcohol until it showed the constant melting-point, 81°–82°, when it was dried *in vacuo*, and analyzed with the following result:

[1] This JOURNAL, 12, 294.

I. 0.1236 gram of the substance gave, by the method of Carius, 0.0684 gram of argentic bromide.

II. 0.2500 gram of the substance gave 18.4 cc. of nitrogen at a temperature of 23° and a pressure of 754.7 mm.

	Calculated for $C_6HBr(C_2H_5O)_2(NO_2)_2$.	Found. I.	II.
Br	23.89	23.56	....
N	8.36	....	8.24

The substance is therefore a bromdinitroresorcine diethylether formed from the trichlorbromdinitrobenzol by the replacement of two atoms of chlorine by ethoxy groups, and of the third by hydrogen. Certain points in regard to its constitution are settled, since the two ethoxy groups must be in the meta position to each other, and the atom of bromine and the two nitro groups are in the symmetrical position to each other. The radicals therefore are probably arranged as follows:

$$(C_2H_5O)_2,1,3,Br2,(NO_2)_2,4,6;$$

but it is possible that one of the ethoxy groups instead of the atom of hydrogen, stands at 5 between the two nitro groups. It is isomeric with the bromdinitroresorcine diethylether melting at 184°, and made by Warren and one of us[1] from tribromdinitrobenzol and sodic ethylate in the cold, which has the constitution $(C_2H_5O)_2,1,5,Br3,(NO_2)_2,2,4$, and also with that melting at 92° obtained by Koch and one of us,[2] as another product from the same reaction, which has the constitution

$$(C_2H_5O)_2,1,3,Br5,(NO_2)_2,2,4.$$

The yield of the bromdinitroresorcine diethylether was 1 gram from 5 of the trichlorbromdinitrobenzol; that is, about 21 per cent of the theoretical yield.

Properties of Bromdinitroresorcine Diethylether, melting at 81°–82°, $C_6H(C_2H_5O)_2Br(NO_2)_2$.

It forms, when crystallized from alcohol, white needles or slender prisms terminated by two planes at an obtuse angle to each other, which turn brown on exposure to the light. It melts at 81°–82°, and is very soluble in benzol, or chloroform; soluble in methyl alcohol, acetone, glacial acetic acid,

[1] This JOURNAL, 13, 167. [2] *Ibid.*, 21, 510.

or carbonic disulphide; slightly soluble in cold ethyl alcohol, more soluble in hot; slightly soluble in ligroin. Alcohol is the best solvent for it. It is not acted on apparently by strong hydrochloric acid, either hot or cold; strong sulphuric acid does not act in the cold, but when warm dissolves it with a brownish red color; strong nitric acid does not act in the cold but gives a colorless solution with it when hot.

That this bromdinitroresorcine diethylether was not the only organic product of the reaction of sodic ethylate on trichlorbromdinitrobenzol was shown by the fact that sodic nitrite as well as sodic chloride was formed. Our attempts to isolate these other bodies, however, were far from successful. Some experiments with the aqueous wash-waters seemed to indicate that they contained a phenol melting at 111°, and having perhaps the formula $C_6(OC_2H_5)_2OH(NO_2)_2Br$, but the analytical data obtained were too imperfect to justify a description of the body; and we did not succeed in bringing any of the other products into a state fit for analysis.

The trichlorbromdinitrobenzol seemed to give colored compounds with sodic ethylate similar to those given by picryl chloride and several other nitro compounds, since upon adding an alcoholic solution of sodic ethylate to the dry substance it took on a strong vermilion color, which was instantly destroyed by water, and more slowly by benzol or ligroin. The fact that the color disappeared on the addition of water indicates that it is one of the colored compounds under discussion, and not a salt of a phenol. Another sample of the substance was allowed to stand for half an hour exposed to the air, at the end of which time the red color had given place to yellow. As the colored compound was less stable than several others which have been studied, its investigation was not carried further.

The trichlorbromdinitrobenzol is acted on by an alcoholic solution of sodium malonic ester. Our first experiments gave a crystalline product, but in too small quantity for analysis. Our later experiments have yielded only viscous masses, from which we have not succeeded in obtaining anything for analysis in spite of a very large expenditure of time and material.

NARCOTINE AND NARCEINE.

By George Bell Frankforter and Frank H. Keller.

In 1888, Roser, in an important paper on narcotine, obtained from narcotine-methyl iodide by a complex process, a base which closely resembled the alkaloid narceine both in physical and chemical properties. Owing to the apparent difference of 1 molecule of water, the substance was called pseudonarceine. Its formation can be represented by the following equation:

$$C_{23}H_{29}NO_7 + CH_3I = C_{23}H_{32}NO_7I.$$

By converting the above iodide into the chloride and treating with an alkali, the chlorine was replaced by the hydroxyl group, forming narcotine-methyl hydroxide:

$$C_{23}H_{32}NO_7I + NaOH = C_{23}H_{32}NO_7OH + NaI.$$

This narcotine-methyl hydroxide, when warmed by passing steam into the solution, or allowing to stand for some time, changes into the so-called pseudonarceine.

While these reactions appear comparatively simple, what actually takes place in the above treatment is quite the opposite. Besides this base, which has since been identified as narceine, a second substance is formed, which was identified by Roser as dimethyltoluene azammonium silver iodide,

$$C_7H_6(CH_3)_2N_2I.2AgI.^2$$

This strange reaction led to a careful examination of the above substance. While in general it does resemble the azimido compounds of Zincke and Lawson, a number of analyses were made without obtaining satisfactory results. A careful comparison of the two substances showed that they were similar, in so far as they were insoluble in nearly all common solvents. The product of Zincke and Lawson was soluble in aniline, nitrobenzene, quinoline, and a strong solution of sodium hyposulphite, from which it was obtained in well-crystallized form. The substance from narcotine proved to be insoluble in cold nitrobenzene, but slightly soluble in

[1] Ann. Chem. (Liebig), **247**, 167. [2] *Ibid.*, **240**, 128.

hot, changing color from a light gray to a light lemon-yellow. On cooling, the yellow color immediately disappeared and the substance was precipitated as an amorphous mass. There was no indication of the formation of a double salt when treated with aniline. In fact, this same yellow substance was obtained from nitrobenzene, aniline, and quinoline. The substance from narcotine melted at 184°–186° C. The compound of Zincke and Lawson melted at 128°–130° C. Neither substance contained water of crystallization.

Analyses of the substance from narcotine gave the following results:

I. 0.1937 gram substance gave 0.1279 gram CO_2, and 0.0316 gram H_2O.

II. 0.2162 gram substance gave 0.1413 gram CO_2, and 0.0345 gram H_2O.

III. 0.2112 gram substance gave 0.1364 gram CO_2, and 0.0333 gram H_2O.

IV. 0.2361 gram substance gave 0.1729 gram AgI.

V. 0.4016 gram substance gave 0.0235 gram N.

	Calculated for $C_7H_8(CH_3)_3N_3I.2AgI$.	Found. I.	II.	III.	IV.	V.
C	14.23	18.00	17.82	17.61	....	....
H	1.58	1.8	1.77	1.75	....	....
N	5.53	....	....	....	....	4.99
I	50.20	....	....	....	39.54	....

The substance from which the above analyses were made was prepared at different times and purified by treating with absolute alcohol and ether. The wide difference between the calculated results and the results of the analyses make it doubtful if these two substances are identical. In fact, it is doubtful if the formula given by Zincke and Lawson[1] is correct as is indicated by the single analysis made by them. If this substance is an azimido compound, it probably contains both iodine and chlorine, one-third of the iodine having been replaced by chlorine. Such a formula agrees very much better with the analyses than does the formula above given.

[1] Zincke and Lawson made one simple determination of silver iodide, obtaining 66.3 per cent. The theoretical is only 61.9.

	Calculated for $C_7H_8(CH_3)_2N_2Cl_2AgI$.	Found. I.	II.	III.	IV.	V.
C	16.19	18.00	17.82	17.61	....	....
H	1.8	1.8	1.77	1.75	....	....
N	6.29	....	....	....	4.99	....
Cl+I	43.37	....	....	....	....	39.54

This mixed formula is strongly supported by recent experiments which indicate the existence of narcotine compounds containing both chlorine and iodine.

The Conversion of Narcotine into Narceine.

As above mentioned, the process of converting narcotine-methyl iodide into the chloride, then into the hydroxide, and finally the latter, by intermutation, into narceine, involves a complex reaction whereby a large percentage of the chloride is converted into the azimido compound. By actual experiment, over 70 per cent of the narcotine-methyl iodide was lost. This fact was an incentive to search for a method by which a larger percentage of the narcotine could be converted into narceine. An examination showed that the loss occurred by treating with silver chloride. Direct substitution of iodine for chlorine was tried, and found to give very satisfactory results.

The following is the method adopted: Narcotine-methyl iodide was made by digesting narcotine with an excess of methyl iodide for ten hours. The excess of methyl iodide was then evaporated off on a water-bath and the residue dissolved in alcohol. The solution was treated with chlorine water. A light yellow substance was formed which was almost immediately dissolved in the alcohol. Upon addition of more chlorine water, more of the yellow substance was precipitated. With a slight excess of the reagent, the precipitate appeared to grow darker in color, and on standing a few minutes, the precipitate collected in flakes, and settled on the bottom, leaving the supernatant liquid with a brownish tinge. On warming for two or three hours, more of the precipitate dissolved, changing the liquid to a dark brown color. When the precipitate was first formed, no signs of crystallization were observed. However, on warming and allowing to stand for several hours, the precipitate appeared under the micro-

scope as small prismatic needles. These crystals were filtered off, purified, and analyzed. The results of the analysis will be tabulated later on.

Narcotine-methyl chloride is very soluble in water, so that, if formed by the action of chlorine water on the iodide, it must necessarily be in the filtrate. The filtrate was, therefore, evaporated to dryness on a water-bath, a brownish, gum-like substance being left, which slowly changed into a crystalline mass. This substance was subsequently identified as pure narcotine-methyl chloride.

The method was then tried quantitatively with the following results:

I. 2.86 grams narcotine-methyl iodide gave 1.22 grams narcotine-methyl chloride.

II. 3.00 grams of narcotine-methyl iodide gave 1.39 grams narcotine-methyl chloride.

Later experiments have shown that a much larger percentage of the chloride can be obtained by using larger quantities of the iodide, thus reducing the relative loss. Fifty to sixty per cent can be obtained, or double the amount obtained by the old method.

In order to determine the purity of the chloride formed, a part was converted into the platinum double salt and examined. This salt is an amorphous powder, slightly soluble in water, and readily so in alcohol. When dried, it melted at 221° C. An analysis of the dried substance gave the following results:

I. 0.2090 gram double salt gave 0.0319 gram Pt.

II. 0.1946 gram double salt gave 0.0298 gram Pt.

	Calculated for $(C_{22}H_{22}NO_7.CH_3Cl)_2PtCl_4$.	Found. I.	Found. II.
Pt	15.39	15.27	15.31

The pure chloride thus obtained was then converted into narceine by the ordinary method of neutralizing with sodium hydroxide and passing a strong current of steam into the solution. On cooling, the whole solution became an almost solid mass of fine, felt-like crystals, which was readily recognized as narceine. The reaction was almost quantitative.

Narcotine-methyl Triiodide, $C_{22}H_{21}I_3NO_7.CH_3I$.—The formation of the brown substance already referred to, on the addition of chlorine water to the narcotine-methyl iodide, indicated that the change from the iodide to the chloride was not by direct substitution. In order to determine, as far as possible, the nature of the reaction, this by-product was examined. When first formed, it was of a dark brown color, and melted at 146° C., but, when recrystallized from alcohol and dried, it melted sharply at 149° C. The purified substance is almost insoluble in cold water, but soluble with difficulty in hot water. It dissolves readily in methyl and ethyl alcohols, from which it crystallizes in fine needles. It is likewise very soluble in chloroform, but, on evaporation, forms a brownish-red varnish. It is slightly soluble in ether and insoluble in carbon disulphide. The substance contains no water of crystallization. Analyses gave the following results :

I. 0.2082 gram of the substance gave 0.2583 gram CO_2, and 0.0633 gram H_2O.

II. 0.2473 gram substance gave 0.3081 gram CO_2, and 0.0723 gram H_2O.

III. 0.1995 gram substance gave 0.1754 gram AgI.

IV. 0.2036 gram substance gave 0.1803 gram AgI.

	Calculated for $C_{23}H_{24}I_4NO_7.CH_3I$.	Found. I.	II.	III.	IV.
C	34.25	33.83	33.98	....	....
H	2.98	3.38	3.25	....	....
I	47.12	....	....	47.50	47.84

From the large percentage of iodine found, it is evident that the iodine of the narcotine-methyl iodide has been concentrated in this by-product, three molecules, in the presence of chlorine, forming two of the chloride and one of the triiodide, according to the following equation :

$$3C_{22}H_{21}NO_7.CH_3I + 2Cl_2 = 2C_{22}H_{23}NO_7.CH_2Cl + C_{22}H_{21}I_3NO_7.CHI_3 + 2HCl.$$

The formation of hydrochloric acid in this reaction accounts for its presence in the liquid. According to the equation, three molecules of the narcotine-methyl iodide should give two molecules of narcotine-methyl chloride, or about 66 per

cent, and one of the triiodide, or 33 per cent. The following determinations verify this equation :

I. 3 grams narcotine-methyl iodide gave 0.979 gram triiodide ; and 1.390 grams narcotine-methyl chloride.

II. 5 grams of narcotine-methyl iodide gave 1.64 grams of triiodide ; and 2.62 grams narcotine-methyl chloride.

As will be seen from the above equation, the highest per cent of the chloride obtainable, is 66, while by the silver chloride method, the formation of the azimido compound, makes only 25 per cent possible.

Methylnornarcotine-methyl Triiodide, $C_{20}H_{17}I_3NO_7.CH_3I$.— Repeated attempts to convert the triiodide into narcotine-methyl chloride were unsuccessful. It was noticed, however, while treating the triiodide with excess of chlorine water, that the melting-point of the brown precipitate was raised, and especially when heated on a water-bath with a large excess of chlorine. A maximum melting-point of 188° C. was finally reached.

According to Matthiessen and Foster,[1] concentrated hydrochloric acid converts narcotine into methylnornarcotine, liberating free methyl chloride. Inasmuch as a large amount of hydrochloric acid was liberated on treating the triiodide with strong chlorine water, it was suspected that this same reaction took place here. In order to examine this reaction more carefully, the following experiment was made : Ten grams of narcotine-methyl iodide were dissolved in a small quantity of alcohol and 200 cc. of strong chlorine water were added. Narcotine-methyl triiodide was formed. The whole mass was then placed on a water-bath and 600 cc. of strong chlorine water were added, a few cubic centimeters at a time. The heating was continued for twelve hours. At the end of that time the substance somewhat resembled the triiodide, except, perhaps, that it was a little darker. It was filtered off and recrystallized from alcohol. The crystals which first formed were of a reddish-brown color and belonged to the monoclinic system. These crystals, recrystallized from alcohol, melted sharply at 186° C. They are soluble in alcohol and chloroform, but insoluble in ether and petroleum ether.

[1] J. Chem. Soc. (London), 21, 357.

Analyses of the dried substance gave the following:

I. 0.2444 gram substance gave 0.2887 gram CO_2, and 0.0729 gram H_2O.

II. 0.2222 gram substance gave 0.2634 gram CO_2, and 0.0609 gram H_2O.

III. 0.2099 gram substance gave 0.1901 gram AgI.

	Calculated for $C_{20}H_{27}I_2NO_7.CH_3I$.	Found. I.	II.	III.
C	32.34	32.22	32.32	....
H	2.57	3.31	3.30	....
I	48.90	....	....	48.93

It would therefore appear that chlorine water acts upon narcotine-methyl triiodide just as hydrochloric acid acts upon narcotine, removing two methoxyl groups from the opianic acid radical, but leaving the third, in the isoquinoline, unchanged. The reaction may be thus represented:

$$C_{19}(OCH_3)H_4I_2N\begin{cases}CH_3\\ -CH_2-CO.C_6H_2\begin{cases}OCH_3\\ OCH_3\\ OCH_3\end{cases}\\ I\end{cases} + 2HCl =$$

$$C_{19}(OCH_3)H_6I_2N\begin{cases}CH_3\\ -CH_2-CO-C_6H_2\begin{cases}OH\\ OH\\ CHO\end{cases}\\ I\end{cases} + 2CH_3Cl.$$

THE REACTION BETWEEN ALIPHATIC SULPHOCYANATES AND METALLIC DERIVATIVES OF ACETOACETIC ESTER AND ANALOGOUS SUBSTANCES.

By Elmer P. Kohler.

The aliphatic sulphocyanates react in a remarkably smooth and clean way with a number of substances which eliminate or replace the cyanogen group. The most important of these reactions are expressed by the following equations:

I. $2C_2H_5SCN + 2Na = (C_2H_5S)_2 + 2NaCN$;

II. $2C_2H_5SCN + K_2S = (C_2H_5S)_2 + KCN + KSCN$;

III. $2C_2H_5SCN + 2KOH = (C_2H_5S)_2 + KCN + KCNO + H_2O$;

IV. $C_2H_5SCN + 2NaSH = C_2H_5SNa + NaCN + H_2S$;

V. $C_2H_5SCN + NaSC_2H_5 = (C_2H_5S)_2 + NaCN$.

In all of these cases and in all other transformations of the sulphocyanates that have hitherto been studied, the cyanogen group is eliminated as the metallic cyanide or cyanate. In the reaction between the sulphocyanates and the metallic derivatives of the esters of ketonic acids the opposite takes place. In this case the primary reaction always results in the formation of a mercaptide and a cyanogen substitution-product of the ester:

$$CH_3COCNa(C_2H_5)CO.OC_2H_5 + C_2H_5SCN =$$
$$CH_3COC(CN)(C_2H_5)CO.OC_2H_5 + C_2H_5SNa.$$

The final result depends, to some extent, upon the ester, the metal, and the sulphocyanate. If the resulting mercaptide is soluble in the liquid used as a medium, it immediately reacts with unchanged sulphocyanate:

$$C_2H_5SCN + NaSC_2H_5 = (C_2H_5S)_2 + NaCN.$$

The final result in the case of sodium ethylacetoacetic ester and ethyl sulphocyanate in absolute alcohol is, therefore, represented by the equation:

$$CH_3COCNa(C_2H_5)CO.OC_2H_5 + 2C_2H_5SCN =$$
$$CH_3COC(CN)(C_2H_5)CO.OC_2H_5 + (C_2H_5S)_2 + NaCN.$$

In case the cyanogen derivative formed in the primary reaction contains hydrogen that is replaceable by metals, it passes into a metallic derivative by liberating a corresponding amount of the original ester; as the cyanogen compounds are invariably more strongly acid than the substances from which they are derived. With sodium acetoacetic ester, in absolute alcohol, for example, the reaction takes place according to the equation:

$$2CH_3COCHNaCO.OC_2H_5 + 2C_2H_5SCN = CH_3COCNa(CN)CO.OC_2H_5 + CH_3COCH_2CO.OC_2H_5 + (C_2H_5S)_2 + NaCN.$$

With sodium derivatives there are further complications due to the fact that sodium mercaptides, like sodium alcoholates, slowly saponify both the original esters and the cyanogen derivatives resulting from the reaction. In these cases the yield of cyanogen ester, under the most favorable circumstances, does not exceed 65 per cent of the amount calculated from the above reactions.

With the copper derivatives the reactions are perfectly clean, as the copper mercaptides are insoluble in organic liquids and inert. The reaction between copper acetoacetic ester and ethyl sulphocyanate, for example, takes place quantitatively, according to the equation:

$$4(CH_3COCHCO.OC_2H_5)_2Cu + 4C_2H_5SCN = 2(CH_3COC(CN)CO.OC_2H_5)_2Cu + 4CH_3COCH_2CO.OC_2H_5 + (C_2H_5S)_2 + 2C_2H_5SCu.$$

This equation may be separated into the following stages:

I. The primary reaction,

$$(CH_3COCHCO.OC_2H_5)_2Cu + 2C_2H_5SCN = 2CH_3COCH(CN)CO.OC_2H_5 + (C_2H_5S)_2Cu.$$

II. Because cyanacetoacetic ester is much more strongly acid than acetoacetic ester,

$$(CH_3COCHCO.OC_2H_5)_2Cu + 2CH_3COCHCNCO.OC_2H_5 = (CH_3COC(CN)CO.OC_2H_5)_2Cu + 2CH_3COCH_2CO.OC_2H_5.$$

III. Because cupric compounds with copper in direct union with sulphur are unstable,

$$\left.\begin{matrix}2C_2H_5S\\C_2H_5S\end{matrix}\right\rangle Cu = 2C_2H_5SCu + C_2H_5S{-}SC_2H_5.$$

The reaction between copper derivatives and polysulphocyanates that have but one sulphocyanogen group with any one carbon atom, normally involves only one of the sulphocyanogen groups; the remainder are protected by the insolubility of the resulting mercaptide. Ethylene sulphocyanate and copper acetoacetic ester, for example, in the cold, react according to the equations:

$$\text{I. } (CH_2COCHCO.OC_2H_5)_2Cu + \begin{matrix} 2CH_2SCN \\ | \\ CH_2SCN \end{matrix} =$$

$$2CH_2COCH(CN)CO.OC_2H_5 + \left(\begin{matrix} CH_2SCN \\ | \\ CH_2S \end{matrix}\right)_2 Cu;$$

$$\text{II. } \left(\begin{matrix} CH_2SCN \\ | \\ CH_2S \end{matrix}\right)_2 Cu = \begin{matrix} 2CH_2SCN \\ | \\ CH_2S\text{–}Cu \end{matrix} + \begin{matrix} CH_2SCN \\ | \\ CH_2\text{–}S\text{–}S\text{–}CH_2 \end{matrix} \begin{matrix} CH_2SCN \\ | \\ \end{matrix}.$$

The sulphocyandisulphides thus formed are soluble in organic solvents, and at higher temperatures react like simpler polysulphocyanates. By adding the sulphocyanate, in very small quantities, to a saturated solution of the copper derivatives, all of the sulphocyanogen groups can be brought into reaction:

$$8(CH_2COCHCO.OC_2H_5)_2Cu + 4C_2H_2(SCN)_2 =$$
$$4(CH_2COC(CN)CO.OC_2H_5)_2Cu +$$
$$8CH_2COCH_2CO.OC_2H_5 + \begin{matrix} 2CH_2SCu \\ | \\ CH_2SCu \end{matrix} + \begin{matrix} CH_2S.SCH_2 \\ | \\ CH_2S.SCH_2 \end{matrix}.$$

When polysulphocyanates have two sulphocyanogen groups in combination with the same carbon atom, both of them enter into reaction under all conditions.

A difference in the behavior with copper and sodium derivatives is observed in the case of halogen substitution-products of the sulphocyanates. With the former, chlorethylsulphocyanate reacts exactly like ethylsulphocyanate—the halogen does not enter into the reaction. With the latter, two reactions take place side by side—the normal reaction of the sulphocyanates and the general reaction of halogen substitution-products:

$$CH_2COCHNaCO.OC_2H_5 + \begin{matrix} CH_2Cl \\ | \\ CH_2SCN \end{matrix} =$$
$$\begin{matrix} CH_2COCHCO.OC_2H_5 \\ | \\ CH_2CH_2SCN \end{matrix} + NaCl.$$

I. Copperacetoacetic Ester and Ethylsulphocyanate.

Sixteen grams (1 molecule) of pure copper acetoacetic ester

were dissolved in 500 cc. of boiling absolute alcohol; 4.5 grams (1 molecule) of ethyl sulphocyanate were added to this and the mixture heated in a water-bath. The solution almost immediately changed from the deep yellow-green color of copper acetoacetic ester to a light blue, and a curdy, cream-colored precipitate began to separate. After boiling for an hour the contents of the flask were almost solid. The liquid was drawn off as rapidly as possible and the boiling continued, but there was no further change.

The yellow precipitate was extracted with boiling absolute alcohol until the extract remained colorless. All the alcoholic solutions were then united, distilled to 500 cc. and allowed to cool. A dark-green copper compound crystallized out in small plates. The substance was washed with alcohol, dried at 100°, and analyzed without further purification:

I. 0.2354 gram substance gave 0.3940 gram CO_2, 0.0953 gram H_2O, and 0.0500 gram CuO.

II. 0.5145 gram substance gave 36.6 cc. N_2 at 16° and 753 mm.

III. 0.4555 gram substance gave 31.2 cc. N_2 at 15° and 753 mm.

	Calculated for $(C_7H_9O_2N_2)Cu$.	Found. I.	II.	III.
C	45.3	45.6	..	..
H	4.3	4.3	..	..
N	8.3	...	8.2	8.0
Cu	17.0	17.0	..	..

The substance is pure coppercyanacetoacetic ester. It is difficultly soluble in boiling alcohol, benzene, acetone, ether, and carbon bisulphide. From a solution in any of these solvents it separates almost completely on cooling. It is insoluble in water and unlike copper acetoacetic ester, is not decomposed when boiled with water or aqueous alcohol. When heated in a capillary tube it remains unchanged until a temperature of about 250° is reached, when it melts with decomposition.

To liberate the ester the salt was warmed with dilute sulphuric acid and a little alcohol. The ester separated as a colorless liquid, which solidified on cooling. The melting-

point of the solid was 26°, as found by Haller and Held.[1]

The light yellow precipitate was washed with ether and dried at 50°.

I. 0.2112 gram substance gave 0.1335 gram CuO.

II. 0.2214 gram substance gave 0.1395 gram CuO.

	Calculated for C_4H_4SCu.	Found. I.	II.
Cu	50.1	50.7	50.5

The substance is copper mercaptide. The high percentage of copper is due to a partial decomposition into mercaptan and copper hydroxide. It gave mercaptan when warmed with concentrated hydrochloric acid, and ethyl disulphide, boiling at 151°, when shaken with iodine and water.

The filtrate from the copper cyanacetoacetic ester was returned to the flask and all the alcohol removed by distillation. The residue was a thick liquid in which some of the copper compound was suspended. The liquid was drawn off and distilled. The temperature rapidly rose to 149°, where all of the liquid passed over. It was ethyl disulphide easily recognized by its boiling-point and the disulphide reaction.

All the alcoholic distillates were combined, fractioned with a Glinsky tube, and the last fraction and the residue treated with ammoniacal copper acetate. Copper acetoacetic ester separated on dilution with water, showing that acetoacetic ester is liberated during the reaction.

The four substances described are always formed when copper acetoacetic ester reacts with ethyl sulphocyanate, and they are the only products of the reaction. 64 grams of copper acetoacetic ester gave 33 grams of copper cyanacetoacetic ester and 11 grams of copper mercaptide. The equation given in the introductory part requires 34.8 grams of the former and 12 grams of the latter.

The course of the reaction cannot be changed by varying the relative amounts of the reacting substances or the conditions. The reaction takes place slowly in the cold, rapidly on heating. Any indifferent solvent may be used as a medium. Ordinary alcohol may be used if the temperature is kept below 70°. Above this point copper acetoacetic ester is rapidly

[1] Ann. Chim. Phys. (6), 17, 204; Traube (Ber. d. chem. Ges., 31, 3587) gives 36°, but this is probably a printer's error.

decomposed by aqueous alcohol, apparently forming an oxy-compound analogous to the ethoxy compounds recently described by Wislicenus.[1]

Methyl sulphocyanate, propyl sulphocyanate, isopropyl sulphocyanate, and benzyl sulphocyanate react like ethyl sulphocyanate. The reaction is, therefore, probably a general one for all aliphatic monosulphocyanates.

II. Copper Acetoacetic Ester and Ethylene Sulphocyanate.

Sixteen grams of copper acetoacetic ester (1 molecule) were gradually added to 15 grams of ethylene sulphocyanate (1 molecule), dissolved in cold absolute alcohol. At first only a grayish-white precipitate separated. After a few days copper cyanacetoacetic ester began to crystallize out along with the white substance. The separation continued slowly for three weeks, when the solution was almost colorless. The liquid was then filtered and the solid extracted with boiling absolute alcohol, which dissolved 8 grams of copper cyanacetic ester. The white residue, after extraction, was dried at 75° and analyzed.

I. 0.2421 gram substance gave 0.1770 gram CO_2, 0.0479 gram H_2O, and 0.1053 gram CuO.

II. 0.4220 gram substance gave 29.3 cc. N_2 at 17° and 755 mm.

III. 0.4515 gram substance gave 31.7 cc. N_2 at 17° and 756 mm.

	Calculated for $C_3H_4I_2NCu$.	Found. I.	II.	III.
C	19.74	19.9	..	..
H	2.02	2.2	..	..
N	7.7	...	8.0	8.1
Cu	35.02	34.8	..	..

The substance is a mixed mercaptide and sulphocyanate of ethane. It is insoluble in water and organic solvents. When boiled with alcoholic potassium sulphide it gives potassium sulphocyanate, proving the presence of the sulphocyanogen group. When boiled with concentrated hydrochloric acid it slowly dissolves as iminomethene-ethene disulphide hydrochloride:

[1] Ber. d. chem. Ges., 31, 3151.

$$\begin{matrix}CH_2SCN\\|\\CH_2SCu\end{matrix} + 2HCl = \begin{matrix}CH_2S\\|\\CH_2S\end{matrix}\!\!>CNH.HCl + CuCl.$$

Fuming nitric acid oxidizes it to (1,2)-ethanedisulphonic acid.

The filtrate from the solid reaction-products was distilled from a water-bath to remove the alcohol, then with superheated steam to remove the acetoacetic ester. There remained a small quantity of unused sulphocyanate suspended in a thick colorless oil. The former was removed by repeated extraction with boiling water, the oil separated and dried over phosphorus pentoxide in a vacuum.

I. 0.3261 gram substance gave 0.3611 gram CO_2, and 0.1026 gram H_2O.

II. 0.3005 gram substance gave 0.3312 gram CO_2, and 0.0945 gram H_2O.

III. 0.4100 gram substance gave 42.7 cc. N_2 at 16° and 750 mm.

IV. 0.3112 gram substance gave 32.5 cc. N_2 at 16° and 750 mm.

	Calculated for $C_4H_8O_4N_2$.	Found. I.	II.	III.	IV.
C	30.51	30.2	30.1	...	...
H	3.39	3.5	3.5	...	...
N	11.9	...	...	12	12.2

The substance is a colorless liquid which does not solidify at —20° and does not boil without decomposition. It is insoluble in water, moderately soluble in boiling alcohol and boiling benzene. It can readily be made in quantity by shaking the mercaptide, above described, with water and iodine:

$$\begin{matrix}2CH_2SCN\\|\\CH_2SCu\end{matrix} + 4I = \begin{matrix}CH_2SCN\\|\\CH_2S\end{matrix}\!\!-\!\!S\!\!-\!\!\begin{matrix}CH_2SCN\\|\\CH_2\end{matrix} + 2CuI_2.$$

This proves that the substance is sulphocyanethyl disulphide. When warmed with strong potassium hydroxide it passes smoothly into ethylene tetrasulphide:

$$\begin{array}{l} CH_2SCN \quad NCSCH_2 \\ | \qquad\quad | \\ CH_2{-}S{-}S{-}CH_2 \end{array} + 2KOH =$$

$$\begin{array}{l} CH_2S{-}S{-}CH_2 \\ | \qquad\quad | \\ CH_2S{-}S{-}CH_2 \end{array} + KCN + KCNO + H_2O.$$

Sulphocyanmethyl disulphide does not react with copper acetoacetic ester in the cold. At the temperature of boiling alcohol the two react to form coppercyanacetoacetic ester and a mixture of complex sulphur compounds that are insoluble in all solvents. It was impossible to separate any pure substances from this mixture; but the amount of copper cyanacetoacetic ester obtained shows that only one of the sulphocyanogen groups is attacked. The reaction is, therefore, similar to that with ethylene sulphocyanate. This explains what happens when the alcoholic solution of 1 molecule of ethylene sulphocyanate and 1 molecule of copper acetoacetic ester is boiled—the disulphide reacts as fast as formed and the final result is copper cyanacetoacetic ester, which can be extracted with alcohol, the copper salt of sulphocyanethylmercaptan, which can be removed with boiling hydrochloric acid, and the complex mixture just described.

If 1 molecule of ethylene is very gradually added to 2 molecules of copper acetoacetic ester in boiling absolute alcohol both of the sulphocyanogen groups enter into the reaction:

$$8(CH_3COCHCO.OC_2H_5)_2Cu + 4C_2H_4(SCN)_2 = \begin{array}{l} CH_2S.SCH_2 \\ | \qquad\quad | \\ CH_2S.SCH_2 \end{array} +$$

$$2C_2H_5S_2Cu_2 + 4\left(\begin{array}{l} CH_3COCCO.OC_2H_5 \\ | \\ CN \end{array}\right)_2Cu +$$

$$8CH_3COCH_2CO.OC_2H_5.$$

Sixteen grams of copper acetoacetic ester were dissolved in 1000 cc. boiling absolute alcohol and 7 grams of ethylene sulphocyanate, likewise dissolved in 1000 cc. absolute alcohol, added drop by drop. After boiling for ten hours the liquid was filtered. The alcoholic solution contained only copper cyanacetoacetic ester and acetoacetic ester. The light yellow solid, insoluble in alcohol, was digested with concentrated hy-

drochloric acid for five hours and the solution distilled with steam. Pure ethylene mercaptan was obtained. The residue insoluble in hydrochloric acid was ethylene tetrasulphide, melting at 151°, and in every respect identical with a specimen prepared by warming ethylene sulphocyanate with a strong solution of potassium hydroxide.

(1,2)-Disulphocyanpropane and (1,3)-disulphocyanpropane react like (1,2)-sulphocyanethane.

III. Copper Acetoacetic Ester and Methylene Sulphocyanate.

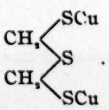
Six and a half grams of methylene sulphocyanate were added to 16 grams of copper acetoacetic ester dissolved in absolute alcohol. No reaction took place in the cold. On warming, a dark brown precipitate formed. After boiling for five hours the liquid was filtered, the precipitate extracted with boiling alcohol, and dried on a water-bath. The alcoholic solution contained 8.2 grams of copper acetoacetic ester, showing that both of the sulphocyanogen groups had entered into the reaction. An analysis of the precipitate gave the following results:

I. 0.5221 gram substance gave 0.1158 gram CO_2, 0.0474 gram H_2O, and 0.3994 gram CuO.

II. 0.4811 gram substance gave 0.1058 gram CO_2, 0.0304 gram H_2O, and 0.3667 gram CuO.

	Calculated for $CH_2S_2Cu_2$.	Found. I.	II.
C	5.84	6.1	6.0
H	0.97	1.01	0.7
Cu	61.5	61.2	61.0

The substance has the composition of copper methylene-mercaptide and seems to be perfectly homogeneous. It may, however, be a mixture of cuprous sulphide and the mercaptide



This would account for the dark color and the behavior with hydrochloric acid. When the substance is allowed to

stand with concentrated hydrochloric acid, hydrogen sulphide is given off, cuprous chloride goes into solution, and the mercaptide referred to is left as a light yellow, impalpable powder:

0.4044 gram substance gave 0.1378 gram CO_2, 0.0618 gram H_2O, and 0.2542 gram CuO.

	Calculated for $C_8H_4S_2Cu_2$.	Found.
C	9.55	9.3
H	1.59	1.7
Cu	50.7	50.3

IV. Copper Acetoacetic Ester and Chlorethyl Sulphocyanate.

Varying quantities of chlorethyl sulphocyanate were heated with copper acetoacetic ester, to determine whether it is possible to get a reaction according to the equation:

$$(CH_3COCHCO.OC_2H_5)_2Cu + 2CH_2ClSCN = 2CH_3COCHCO.OC_2H_5 + 2CuCl_2.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad C_2H_4SCN$$

In all cases the reaction was the same as with ethyl sulphocyanate. No cuprous chloride could be detected and the amount of copper cyanacetoacetic ester obtained agreed closely with the amount calculated.

V. Sodium Acetoacetic Ester and Ethyl Sulphocyanate.

The reactions with sodium acetoacetic ester are not nearly as clean as those with copper acetoacetic ester as the sodium mercaptide formed, like sodium ethylate, decomposes both the unchanged acetoacetic ester and the cyanacetoacetic ester, which is a product of the reaction. If, for example, acetoacetic ester, sodium alcoholate, and a sulphocyanate are brought together in molecular quantities in absolute alcohol, the yield of cyanacetoacetic ester never exceeds 15 per cent of the amount calculated from the equation:

$$CH_3COCHNaCO.OC_2H_5 + C_2H_5SCN = CH_3COCNaCO.OC_2H_5 + C_2H_5SH.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad CN$$

The by-products are, in this case, sodium acetate and

sodium carbonate from acetoacetic ester, and ethyl disulphide and sodium cyanide formed by the action of sodium mercaptide on the sulphocyanate,

$$C_2H_5SCN + NaSC_2H_5 = (C_2H_5S)_2 + NaCN.$$

A somewhat better yield was obtained by mixing acetoacetic ester with benzene, and alternately adding small quantities of dry sodium alcoholate and ethyl sulphocyanate until the three substances were present in molecular quantities. The mixture was allowed to stand for several days, then poured into water and carefully acidified with dilute acetic acid. The benzene solution contained only ethylmercaptan and a small quantity of ethyl disulphide. The aqueous solution, on evaporation, gave a 32 per cent yield of sodium cyanacetoacetic ester and a small quantity of sodium cyanide.

The best results were obtained by bringing together pure, dry sodium acetoacetic ester and an excess of the sulphocyanate in absolute ether, and allowing the mixture to stand in the cold. 45 grams of ethyl sulphocyanate were added to 75 grams of sodium acetoacetic ester suspended in 750 cc. ether, and the mixture allowed to stand for two weeks. A part of the ether was removed by distillation, the residue poured into water and acidified with acetic acid. After separating the aqueous solution it was acidified with sulphuric acid and repeatedly extracted with small quantities of ether. This ethereal solution, when separated by fractional distillation under diminished pressure, gave 42 grams of cyanacetoacetic ester—a yield of about 60 per cent.

VI. Sodium Ethyl Acetoacetic Ester and Ethyl Sulphocyanate.

In all the experiments hitherto described, one of the products was a metallic derivative of acetoacetic ester. To determine whether the reaction is possible when it involves the formation of an ester which contains no hydrogen replaceable by metals, molecular quantities of ethyl acetoacetic ester, dry sodium alcoholate, and ethyl sulphocyanate were brought together in absolute ether. After standing for two weeks, the resulting mixture was separated and the products purified as in the preceding experiment. A 22 per cent yield of cyan-

ethylacetoacetic ester was obtained. The ester boiled at 130° at a pressure of about 35 mm ; and the analyses show that it was pure.

I. 0.2185 gram substance gave 0.4702 gram CO_2, and 0.1390 gram H_2O.

II. 0.2213 gram substance gave 0.4771 gram CO_2, and 0.1413 gram H_2O.

III. 0.4216 gram substance gave 28.5 cc. N_2 at 17° and 755 mm.

	Calculated for $C_9H_{13}O_3N$.	Found. I.	II.	III.
C	59.01	58.7	58.8	...
H	7.1	6.9	7.1	...
N	7.65	...	...	7.8

VII. Sodium Acetoacetic Ester and Chlorethyl Sulphocyanate.

A solution of sodium acetoacetic ester was prepared by dissolving 11.5 grams of sodium in 200 cc. of absolute alcohol and adding 65 grams of acetoacetic ester. 65 grams of chlorethyl sulphocyanate were added to this solution. The resulting liquid was boiled, with inverted condenser, until the reaction was neutral to litmus. The alcohol was removed and the residue poured into water when a heavy brown oil separated. This was washed with a dilute solution of sodium hydroxide until the washings were colorless. The oil was separated and cooled in ice-water, when most of it solidified. The solid was dried on plates and purified by recrystallization from petroleum ether. It was thus obtained in colorless, transparent plates or needles melting sharply at 83°.

I. 0.3115 gram substance gave 0.5716 gram CO_2, and 0.1678 gram H_2O.

II. 0.4623 gram substance gave 30.2 cc. N_2 at 28.5° and 744 mm.

	Calculated for $C_9H_{13}O_3SN$.	Found. I.	II.
C	50.2	50.1	...
H	6.05	6.0	...
N	6.51	...	6.9

The substance is sulphocyanethylacetoacetic ester, formed according to the equation :

$$CH_3COCHNaCO.OC_2H_5 + ClC_2H_4SCN = CH_3COCHCO.OC_2H_5 + NaCl.$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_2.CH_2SCN$$

The substance is insoluble in water, moderately soluble in petroleum ether, very soluble in alcohol, ether, and benzene. It reacts with copper acetoacetic ester to form copper cyanacetoacetic ester and a mercaptide, proving the presence of a sulphocyanogen group. 30 grams of the substance were obtained from 65 grams of acetoacetic ester.

The aqueous solution, separated from the oil, was decolorized with bone-black and evaporated to crystallization. It gave 38 grams of sodium cyanacetoacetic ester.

BRYN MAWR COLLEGE.
CHEMICAL LABORATORY.

A METHOD FOR CARRYING OUT CHEMICAL REACTIONS UNDER HIGH PRESSURES.

BY B. H. HITE.

The great majority of chemical reactions are carried out under ordinary, or atmospheric, pressures, which happen to be really very low pressures. Even in the comparatively few cases in which somewhat higher pressures are used, as those accomplished in an autoclave or Carius tube, the effect of the pressure cannot be determined on account of the elevation of temperature necessary to obtain the pressure. There is no convenient practical method, certainly none in general use, that is independent of the temperature and applicable to a very wide range of pressures. The lack of such a method or apparatus is the more noticeable in view of the long list of devices available for studying the effect of temperature. That most reactions are far more susceptible to slight changes of temperature than to what might perhaps be regarded as comparable changes in pressure is doubtless true, and it may be that the relative importance of these two agents is indicated fairly enough by the usual laboratory equipment, and yet before taking this for granted it would seem that, inasmuch as available temperatures have been extended to the fusing-point of carbon, there ought to be one method, at least, in which

available pressures would be limited only by the crushing strength of steel.

Such a method should be applicable to reagents in solution, in quantities suitable for experimental purposes, and, if possible, in glass or platinum vessels. There must be no leaking under the pressure applied, which must be absolutely independent of the temperature used. A description of such a method follows:

A platinum tube T, Fig. 1, 4 inches long by $\frac{3}{4}$ inch in

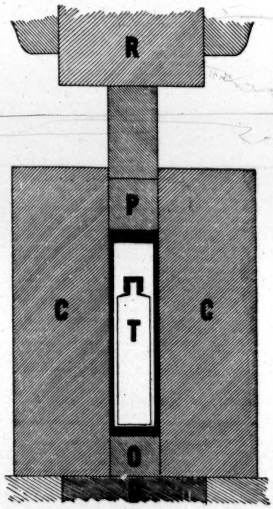


Fig. 1.

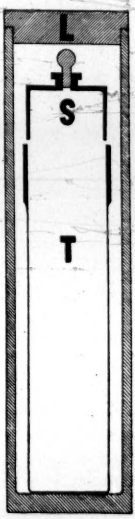


Fig. 2

diameter, and similar generally to the ordinary collapsible lead (or tin) paint tubes is filled with the solution of the reagents, closed with a stopper or screw cap, and placed in a lead tube about $1\frac{1}{4}$ inches in diameter by 5 or 6 inches long. The lead tube (see also Fig. 2) is then filled with water, closed with a lid L, and placed in a steel cylinder C, about 7 inches long by 6 inches in diameter, with a hole through it about $1\frac{1}{4}$ inches in

diameter. The lead tube rests on a steel plug O, which closes the lower end of the cylinder and rests on the bed-plate B, of a powerful hydraulic press, while the pressure exerted by the ram R of the press is communicated by means of a steel piston P to the lead tube and its contents.

The platinum tube simply serves to separate the reagents within from the water surrounding it. It may be made very similar to the collapsible tubes mentioned : indeed these tubes may be very conveniently substituted whenever the reagents to be used will not attack them. Several thousand of these tin tubes were used in studying the effect of pressure on solutions containing bacteria, and found to be entirely satisfactory. The platinum tubes should be made of very thin foil, so that on relieving the pressure the liquid within the tubes, expanding to its original volume, may not injure the screw caps or displace the stopper used in closing the tubes. The wide-mouth tube T, shown in Fig. 2, is a very convenient form, as it is easily filled and emptied, and the dents which have a tendency to accumulate may be easily removed. The walls of this tube are reinforced for about an inch from the mouth to make them firm enough to hold the stopper S, which is provided with a small opening through which may escape any excess of solution, or any air bubbles that might otherwise be enclosed, thus permitting the stopper to be forced securely into the mouth of the tube, when the small opening is closed, as shown, with a small platinum plug.

The lead tube, which is the packing of this device, is securely sealed by the pressure so that *the liquid is completely encased in one continuous piece of metal.* It is this continuous metal packing that is responsible for the high pressures obtainable by this method. On removing the pressure, the water, in expanding to its original volume, will sometimes loosen the lid of the lead tubes, and if a high pressure has been used the lead tube, in stretching to its original capacity, will sometimes be pulled completely in two ; but as nothing but water can escape in either case these are not serious matters. There is absolutely no trace of leak while the liquid is under pressure.

The cylinder C should be made of the very finest tool steel.

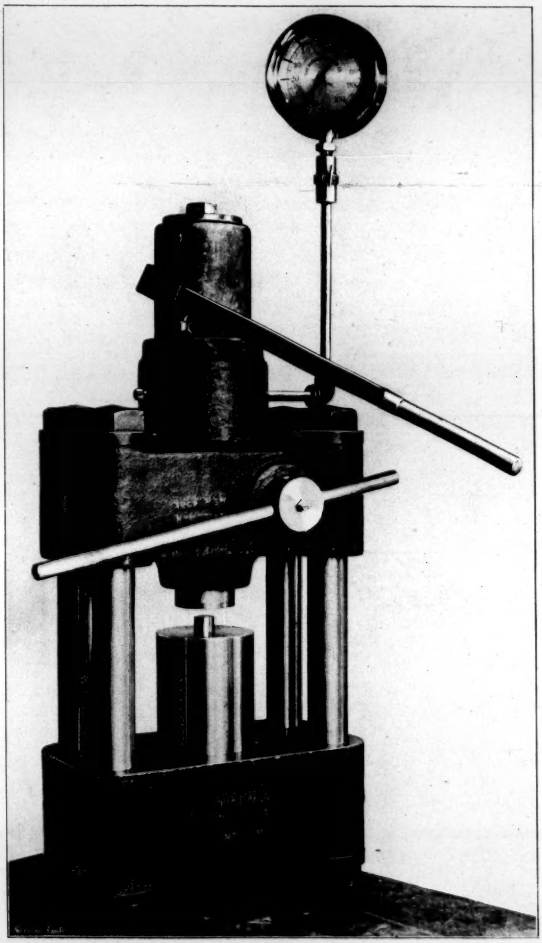


Fig. 3.

The hole through it must be true and smooth, and must fit accurately the plugs or pistons, O and P, which must also be made of the very finest tool steel and tempered hard. Just how hard the cylinder should be tempered seems to depend upon the kind of steel used. The cylinders must be hard enough to keep their shape, and yet if tempered too hard they are likely to contain a number of very fine cracks imperceptible at first, but which will open a little wider with each application of the pressure until the cylinder gives way. The best results were obtained with cylinders made of a special steel which, without much tempering, is hard enough to keep its shape. Most of the cylinders were "built up" of a number of concentric cylinders shrunk together, the object being to make the outer part of the cylinder carry more of the strain than it would if made of one piece.

With cylinders of the dimensions named, reactions have been carried out under a pressure of 200,000 pounds to the square inch, but having forced a cylinder of this size (1¼ inch bore) to such a pressure once, it is by no means safe to conclude that it will stand the same pressure again, for it may burst under a much lower pressure. Even the hard tool steel plugs and pistons have been crushed by such pressures, so it would seem that the limit had been reached, at least for cylinders of this size. If higher pressures are desired, cylinders of smaller bore must be used. A three-fourths inch bore will be found very convenient for pressures of about 200,000 pounds to the square inch. A one-half inch bore is the smallest that has been used by the writer. With cylinders of this size pressures of over 400,000 pounds to the square inch have been obtained, but in such tests the tool steel pistons were completely crushed.

The ram R of the press must be made of hard steel and a block B of the same material should be embedded in the lower platten of the press. The "four-rod, punch-type" hydraulic press, shown in Fig. 3, is a very convenient machine with which to apply and measure the pressures. It weighs about 1,000 pounds and has a capacity of considerably more than 100 tons. The pressure is applied and relieved by means of the upper lever shown in the cut. The ram is quickly raised or lowered with the lower lever.

It will be observed that there is ample room in this press for inclosing the cylinder within a jacket or bath by means of which the effect of a wide range of temperature may be studied in connection with the pressure, and, that the application of each is entirely independent of the other.

A testing machine may be used to furnish and measure the pressure. In order that the method might be applicable to long-continued pressures without being limited to one determination at a time, and without leaving the press so long under a strain, the cylinder shown in Fig. 4 was devised. It is somewhat longer than the one just described, and the bore is abruptly decreased at a point a short distance above the bottom forming a shoulder upon which rests the lower plug O. The piston P is also provided with a shoulder which enables the pressure (after being applied as before) to be carried by the heavy screw S. In order to open this cylinder it will be necessary to put it back into the press and apply enough pressure to the piston to relieve the screw, which is then removed, and the piston, the lead tube, and the plug O are pushed out with a steel rod applied through the hole in the bottom of the cylinder. This cylinder has another advantage, especially when a testing machine is used, in that it may be inverted or shaken so as to mix the reagents while they are under pressure. This is desirable in working with reactions which readily take place under ordinary pressures, but which are suspected of taking a different course under higher pressures. In such cases the reaction should not begin until the pressure

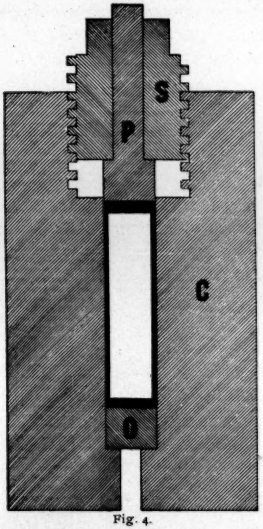


Fig. 4.

is applied. Several methods for accomplishing this will suggest themselves; among them the following: the reagents are dissolved in two separate portions of the solvent, the solution of higher specific gravity poured into the platinum tube first, then the other portion is introduced carefully so as not to mix the two. After the pressure is applied and secured by the screw, the cylinder is inverted. This may, however, be accomplished just as easily in the simpler cylinder first described and with the advantage of an unbroken record of the pressure, if the press is supported so that it may be tilted. Of course, in working with reactions which do not take place until higher pressures or temperatures than ordinary have been applied, no such precautions will be necessary.

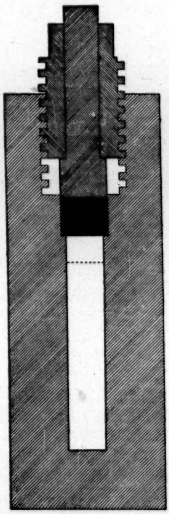


Fig. 5.

A cylinder that may be very conveniently used in many lines of work is shown in Fig. 5. It is made much lighter than those described and is not intended for pressures of more than about 25 tons per square inch. It will be observed that the pressure may be secured by the screw and so continued indefinitely after removing from the press; also that the lower end of the cylinder is permanently closed. In this cylinder a solid block of lead (indicated in the section by the solid rectangle) serves as the packing. It rests on an offset or shoulder, the space below it being filled with water, and the platinum tube containing the reagents. The piston forces the lead down into the cylinder, compressing the water and preventing its escape. In order to open the cylinder the piston and packing must be pulled out. The piston can be easily removed if fastened in a vise. The packing may be removed by a screw, the head of which is held in a vise. These would not be the comparatively easy operations they are, but for the fact that the water in expanding gives the packing and piston a decided start.

One person can open and charge 10 or 12 cylinders in an hour.

A certain amount of pressure is always required to force the lead packing past the shoulder, and in order to measure accurately the net pressure on the water, a hole is drilled through the side of the cylinder, and a piece of tubing leading to a gauge is attached directly. A gauge attached in this way to a cylinder containing a liquid under pressure is extremely sensitive to changes in temperature, and if a constant pressure is to be maintained *after the cylinders are taken from the press*, the temperature must not change. These low pressure cylinders would certainly be convenient substitutes in many cases for autoclaves or sealed tubes. Of course other metals (or alloys) than lead may be used as packing and other liquids than water may be used to communicate the pressure to the platinum tube and its contents.

The above method was worked out in connection with a study of the effect of pressure on bacteria in milk, meats, fruit juices, and other perishable food-stuffs. At odd moments, while this work was going on, the effect of pressure on a number of chemical reactions received attention, and these will be reported in the near future.

WEST VIRGINIA AGRICULTURAL
EXPERIMENT STATION,
MORGANTOWN, W. VA.

NOTE.

A New Test for Cocaine.

There are two well-known tests for determining the freedom of commercial cocaine salts from other coca alkaloids. These are the permanganate test for detecting cinnamyl-cocaine, and the ammonia test, popularly known as McLagan's test, for detecting the presence of the coca alkaloids which are resistant to permanganate.

While it is generally admitted that the permanganate test is sufficient to detect the presence of cinnamyl compounds, chemists have expressed some doubt regarding the value of McLagan's test. The writer has for some time been conducting experiments with the object of finding a substitute for McLagan's test which would allow of the rapid and accurate

determination of the presence in cocaine salts of the coca alkaloids not indicated by the permanganate test.

As the result of numerous determinations, I have devised a test based on the fact that the chromates of these alkaloids are much less soluble than cocaine chromate, both in water and in water acidulated with hydrochloric acid. The relative solubility of the chromates in acidulated water is about 1 to 500 in the case of cocaine chromate, and 1 to 5000 in the case of residual alkaloidal chromates.

I therefore offer the following as a simple and satisfactory method of determining the purity of cocaine salts: 0.05 gram cocaine hydrochloride is dissolved in 20 cc. of distilled water, mixed with 5 cc. of a 3 per cent solution of chromic acid, and to the mixture 5 cc. of a 10 per cent solution of hydrochloric acid are added. It is advisable to keep the temperature of the solution at 15° C. If the cocaine hydrochloride is pure a clear solution will result. If other than traces of foreign coca bases are present the solution becomes cloudy at once, or in a few minutes, according to the amount of impurity present.

It is advisable to make the test side by side with a specimen of known purity for comparison.

GEORGE L. SCHAEFER.

N. Y. QUININE AND CHEMICAL WORKS,
March 27, 1899.

OBITUARY NOTICE.

CHARLES FRIEDEL. (1832–1899.)

In the death of Charles Friedel, at the age of sixty-seven, which occurred April 20th, France lost one of her best known chemists. He manifested a talent for science at an early age, an inheritance perhaps from his grandfather, Dr. Duvernoy, who was a man of scientific attainments, and at the time of his death was recognized as a man well worthy of the high honors which had been bestowed upon him. After taking the degree of B.S., with honors he came under the influence and inspiration of Wurtz. He was made Doctor of Science in 1869, instructor at École Normale Supérieure in 1871, Professor of Mineralogy at the Sorbonne in 1876, Member of the Institute in 1878, and Professor of Chemistry, to succeed Wurtz, in 1884. He was the holder of several honorary degrees from the English Universities and in 1880 he was awarded the Davy Medal by the Royal Society. In him was combined both the skill of the investigator and the inspiring enthusiasm and clear logical presentation of the teacher.

His contributions to science, which have appeared in about 100 papers, relate mainly to organic chemistry. After his first paper, which appeared in 1876 on acetone, he extended the work to other compounds containing three carbon atoms, and also did much to advance the ideas of Kekulé on the structure of carbon compounds. Evidence confirming the views of Kekulé as to the quadrivalence of carbon resulted from his work on silicon and titanium, which he showed were similar in their chemical behavior to carbon and quadrivalents. His name is perhaps best known from his connection with the so-called Friedel-Crafts reaction. These chemists showed that a hydrocarbon residue could be readily introduced into many substances by treating a hydrocarbon with a chlorine derivative in the presence of aluminium chloride. Friedel was also greatly interested in the practical side of chemistry, was the founder of the French Association for the Advancement of Science, and acted as President of the Congress on Chemical Nomenclature which met at Geneva in 1892.

J. E. G.